

# PATENT ABSTRACTS OF JAPAN

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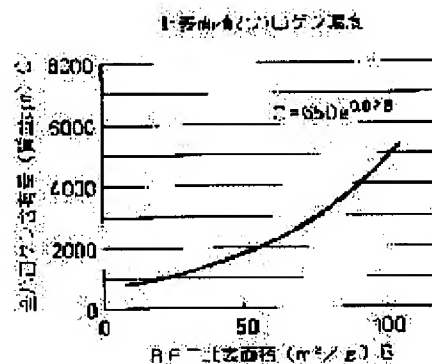
## (54) LOW HALOGEN-LOW RUTILE TYPE HYPERFINE-GRAINED TITANIUM OXIDE AND PRODUCTION METHOD THEREOF

(57)Abstract:

PROBLEM TO BE SOLVED: To provide low rutile type hyperfine-grained titanium oxide which has excellent dispersibility and has a low halogen content in a vapor phase method, and to provide a production method thereof.

SOLUTION: In a vapor phase method where a gas containing titanium halide and an oxidizing gas are reacted, the raw material gases are reacted while controlling heating temperature and heating time, and thereafter, dehalogenation is performed, so that low rutile type hyperfine-grained titanium oxide in which the content of rutile is  $\leq 5\%$ , and having a high BET (Brunauer, Emmett and Teller) specific surface area and specified characteristics is obtained.

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**CLAIMS**

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[Claim(s)]

[Claim 1]Are titanium oxide obtained by making gas and a oxidizing gas containing halogenation titanium react, and rutile content at 5% or less. And when B ( $\text{m}^2/\text{g}$ ) and a total halogen content of titanium oxide are set to C (mass ppm) for specific surface area of titanium oxide measured with a BET one point method for BET method, Titanium oxide when it is shown by  $C \leq 650e^{0.02B}$  and is considered as aqueous suspension of 1 mass %, wherein halogen more than 80 mass % of the amount of halogen contained in titanium oxide after neglect for 30 minutes at 20 \*\* shifts the aqueous suspension to the liquid phase.

[Claim 2]The titanium oxide according to claim 1 in which halogen more than 90 mass % of the amount of halogen contained in titanium oxide shifts to the liquid phase.

[Claim 3]The titanium oxide according to claim 1 or 2 in which titanium oxide contains each element of Fe, aluminum, Si, and S below 100 mass ppm, respectively.

[Claim 4]The titanium oxide according to claim 1 to 3 in which titanium oxide has the specific surface area of 10–200– $\text{m}^2/\text{g}$ .

[Claim 5]The titanium oxide according to claim 1 to 4 whose main phase of titanium oxide is anatase.

[Claim 6]The titanium oxide according to claim 5 whose anatase content of titanium oxide is not less than 90%.

[Claim 7]The titanium oxide according to claim 1 to 4 whose main phase of titanium oxide is brookite.

[Claim 8]Titanium oxide of claim 7 whose brookite content of titanium oxide is not less than 90%.

[Claim 9]Titanium oxide given in any 1 paragraph of claims 1 thru/or 8 in which titanium oxide has a diameter of 90% accumulation mass particle size distribution of 2.5 micrometers or less measured with a laser diffraction type grading analysis meter.

[Claim 10]Titanium oxide given in any 1 paragraph of claims 1 thru/or 9 said whose halogenation titanium is titanium tetrachloride and in which said halogen is chlorine.

[Claim 11]In the gaseous phase method for manufacturing titanium oxide by making gas and a oxidizing gas containing halogenation titanium react, A manufacturing method of titanium oxide in which temperature in this reactor is characterized by not less than 800 \*\* being less than 1,100 \*\* when gas and a oxidizing gas containing halogenation titanium are introduced into a reactor, respectively and are made to react.

[Claim 12]A manufacturing method of the titanium oxide according to claim 11 whose with a not less than 800 \*\* [ temperature below 1,100 \*\* ] holding time gas and a oxidizing gas containing halogenation titanium is 0.1 or less second within a reactor.

[Claim 13]A manufacturing method of the titanium oxide according to claim 11 or 12 in which gas and a oxidizing gas containing halogenation titanium are preheated by not less than 600 \*\* and less than 1,100 \*\*, and are introduced into a reactor, respectively.

[Claim 14]A manufacturing method of titanium oxide given in any 1 paragraph of material gas which a reaction mixed at a rate of 0.1–20 mol of inactive gas to 1 mol of halogenation titanium, and claims 11 thru/or 13 performed with a 1–30–mol oxidizing gas to 1 mol of halogenation titanium.

[Claim 15]A manufacturing method of titanium oxide given in any 1 paragraph of claims 11 thru/or 14, wherein a oxidizing gas is oxygen gas containing a steam.

[Claim 16]A manufacturing method of the titanium oxide according to claim 15 in which a oxidizing gas contains 0.1 mol or more of steams to 1 mol of oxygen gas.

[Claim 17]A manufacturing method of titanium oxide given in any 1 paragraph of claims 11 thru/or 16

in which said halogenation titanium is titanium tetrachloride.

[Claim 18]A manufacturing method of titanium oxide removing halogen for titanium oxide manufactured with a manufacturing method given in any 1 paragraph of claims 11 thru/or 17 by dry type.

[Claim 19]A manufacturing method of the titanium oxide according to claim 18 which is the method of performing when a method of removing halogen by dry type heats titanium oxide at 200–500 \*\*.

[Claim 20]A manufacturing method of the titanium oxide according to claim 18 whose method of removing halogen by dry type is the method of performing while heating gas containing a steam at 200–1000 \*\* and making titanium oxide contact.

[Claim 21]A manufacturing method of the titanium oxide according to claim 20 which is the air in which gas containing a steam contains a steam in more than 0.1 capacity %.

[Claim 22]A manufacturing method of the titanium oxide according to claim 20 whose steam is 0.01 or more in a mass ratio to titanium oxide.

[Claim 23]A manufacturing method of titanium oxide obtaining a slurry which removes halogen for titanium oxide manufactured with a manufacturing method given in any 1 paragraph of claims 11 thru/or 17 by a wet type, and contains titanium oxide.

[Claim 24]A manufacturing method of the titanium oxide according to claim 23 which is the method of separating halogen in which a method of removing halogen by a wet type made titanium oxide suspended in water, and shifted to the liquid phase out of a system.

[Claim 25]A manufacturing method of the titanium oxide according to claim 23 or 24 whose method of removing halogen by a wet type is a method of separating halogen by ultrafiltration membrane.

[Claim 26]A manufacturing method of the titanium oxide according to claim 23 or 24 whose method of removing halogen by a wet type is a method of separating halogen by a reverse osmotic membrane.

[Claim 27]A manufacturing method of the titanium oxide according to claim 23 or 24 whose method of removing halogen by a wet type is a way the filter press separates halogen.

[Claim 28]A granular material by which titanium oxide manufactured with a manufacturing method of a statement being included in any 1 paragraph of claims 11 thru/or 27.

[Claim 29]A slurry by which titanium oxide manufactured with a manufacturing method of a statement being included in any 1 paragraph of claims 11 thru/or 27.

[Claim 30]A constituent by which titanium oxide manufactured with a manufacturing method of a statement being included in any 1 paragraph of claims 11 thru/or 27.

[Claim 31]A photocatalyst material by which titanium oxide manufactured with a manufacturing method of a statement being included in any 1 paragraph of claims 11 thru/or 27.

[Claim 32]A charge of wet solar cell material by which titanium oxide manufactured with a manufacturing method of a statement being included in any 1 paragraph of claims 11 thru/or 27.

[Claim 33]A dielectric raw material by which titanium oxide manufactured with a manufacturing method of a statement being included in any 1 paragraph of claims 11 thru/or 27.

[Claim 34]A silicone rubber additive agent by which titanium oxide manufactured with a manufacturing method of a statement being included in any 1 paragraph of claims 11 thru/or 27.

[Claim 35]Specific surface area which rutile content measured with a BET one point method for BET method 5% or less  $10\text{--}200\text{m}^2/\text{g}$ , A diameter of 90% accumulation mass particle size distribution measured with a laser diffraction type grading analysis meter is a titanium oxide particle of 2.5 micrometers or less, And when a halogen content inside B ( $\text{m}^2/\text{g}$ ) and a titanium oxide particle is made into  $C_i$  (mass ppm) for specific surface area of titanium oxide measured with a BET one point method for BET method, A titanium oxide particle, wherein the amount of halogen contained in an inside of particles is shown by  $0 \leq C_i \leq 650k e^{0.02B}$  (k is 0.20).

[Claim 36]The titanium oxide particle according to claim 35 which contains in an inside of particles halogen of quantity shown by  $10 < C_i \leq 650k e^{0.02B}$  (k is 0.15).

[Translation done.]

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to suitable low-salt matter ultrafine particle titanium oxide of a low rutile type for a photocatalyst, a solar cell, the additive agent to silicone rubber, a dielectric use, etc., and a manufacturing method for the same. In the gaseous phase method titanium oxide obtained by carrying out high temperature oxidation of the gas containing halogen titanium with an oxidizing gas in more detail, it is related with good low halogen ultrafine particle titanium oxide of a low rutile type and a manufacturing method for the same of dispersibility easily [ a halogen content is low and / removal of the halogen which remained ].

[0002]

[Description of the Prior Art]Ultrafine particle titanium oxide has been used [ many uses, such as an ultraviolet-rays shielding material, an additive agent of silicone GOMUHE, a dielectric raw material, and cosmetics, ] (titanium oxide is indicated to be a titanium dioxide to Japanese Industrial Standard (JIS)).

Since titanium oxide is widely used as a general name, in this specification, it is called titanium oxide for short.

Titanium oxide is applied also as a photocatalyst, a solar cell, etc.

[0003]Although a rutile type, an anatase type, and three brookite type kinds exist in the crystal form of titanium oxide, in the above-mentioned photocatalyst and the field of a solar cell use, the anatase type and brookite type which excel a rutile type in photoelectricity chemicals activity are used.

[0004]The photocatalyst effect of titanium oxide is used for disassembly of organic matters, such as an antibacterial tile, self-cleaning building materials, and a deodorizing fiber, and the mechanism is explained as follows. Titanium oxide absorbs ultraviolet rays and makes the inside generate an electron and an electron hole. An electron hole reacts to the water of adsorption of titanium oxide, makes a hydroxy radical generate, and disassembles into carbon dioxide or water the organic matter which stuck to the titanium oxide particle surface ("optical clean revolution" Akira Fujishima, Kazuhito Hashimoto, Toshiya Watabe collaboration, CMC Co., Ltd., 143 - 145 pages (1997)). That is, it being easy to generate an electron hole and arriving [ an electron hole / easily ]-at the titanium oxide surface \*\* are mentioned as conditions for strong titanium oxide of a photocatalyst effect. Anatase type titanium oxide, titanium oxide with few lattice defects, and titanium oxide with large specific surface area with small particles are mentioned to "everything about titanium oxide photocatalysts" (Kazuhito Hashimoto and Fujishima Showa edit, CMC Co., Ltd., 29 - 30 pages (1998)) as titanium oxide with a high photocatalyst effect.

[0005]Since the application as a solar cell reported the dye sensitizing type solar cell with which GURETTSUERU and others of Lausanne College of Engineering combined titanium oxide and ruthenium series coloring matter in 1991, research has been advanced (M. (Graezel, Nature, 353 and 737, 1991)). In said dye sensitizing type solar cell, titanium oxide has a role of the support and the n-type semiconductor of coloring matter, and is used as a coloring matter electrode bound to the electrically-conductive-glass electrode. A dye sensitizing type solar cell is the structure which put the electrolyzer by the coloring matter electrode and the counter electrode, and coloring matter generates an electron and an electron hole by absorbing light. The electron by which it was generated reaches an electrically-conductive-glass electrode through a titanium oxide layer, and is taken out outside. On the other hand, the generated electron hole is carried to a counter electrode through an electrolyzer, and is combined with the electron supplied through the electrically-conductive-glass

electrode. As a cause which improves the characteristic of a dye sensitizing type solar cell, it is mentioned that combination of titanium oxide and coloring matter is easy. As a crystal form of titanium oxide with an easy combination with coloring matter, anatase is used for JP,10-255863,A and it is indicated to JP,2000-340269,A, for example that brookite is suitable for a dye sensitizing type solar cell.

[0006]Titanium oxide is important when the good thing of dispersibility pulls out the function. For example, since obliterating power will become strong if dispersibility is bad when using titanium oxide as a photocatalyst, the use which can be used will be limited. Since titanium oxide with bad dispersibility in the field of a solar cell cannot penetrate light easily, the titanium oxide which can be contributed to optical absorption is restricted, and it worsens photoelectric conversion efficiency. Generally, if light scattering (obliterating power) becomes the maximum when particle diameter is about [ of a visible light wavelength ]  $1/2$ , and particle diameter becomes small, it is said that light scattering also becomes weaker ("titanium oxide" Seino \*\*\*\*, Gihodo Shuppan Co., Ltd., Inc., p.129, (1991)). the primary particle diameter of the titanium oxide used in the above-mentioned field -- number -- since it is tens of nm in many cases, if dispersibility is good, the influence on light scattering is small. However, as for titanium oxide with large condensation particle diameter with bad distribution, light scattering will become strong.

[0007]From the above reason, in the above-mentioned field, high dispersibility is required of titanium oxide and the good anatase type of dispersibility or brookite type ultrafine particle titanium oxide is used for it. Generally, the primary particle diameter of an ultrafine particle is usually called to particle of about 0.1 micrometer or less, although it does not clarify.

[0008]If the ingredient which has corrosiveness like chlorine exists, in order to make a substrate corrode or to make it deteriorate when using titanium oxide with a photocatalyst and a solar cell, it is necessary to stop the chlorine content of titanium oxide low. It is better to stop Fe, aluminum, Si, S, etc. low. For example, if there is too much Fe in titanium oxide, it will become a cause of coloring, and it is not suitable for use for the use of which transparency is required. If there are too many ingredients, such as aluminum inside a titanium oxide particle and S, a lattice defect will be produced, and reducing the function as a photocatalyst and a solar cell is also considered.

[0009]The manufacturing method of titanium oxide has a liquid phase process which divides roughly and hydrolyzes titanium tetrachloride and titanyl sulfate, and the gaseous phase method make halogenation titanium react to oxidizing gases, such as oxygen or a steam. Although titanium oxide by a liquid phase process can obtain anatase as a main phase, it cannot but be in sol or a slurry regime. A use is limited when using it in this state. In order to use it as powder, it is necessary to make it dry, and desiccation takes the ultrafine particle which got wet in the solvent for progressing, and condensation becomes intense ("ultrafine particle handbook" Saito [ Susumu ] 6 editorial supervision, a FUJI techno system, 388 pages (1990)). In presenting a photocatalyst etc. with this titanium oxide, in order to improve dispersibility, it is necessary to crack titanium oxide strongly or to grind, and problems originating in processing of grinding etc., such as mixing of a wear thing and unevenness of particle size distribution, may be caused.

[0010]Generally, since a solvent is not used for titanium oxide by a gaseous phase method, it is excellent in dispersibility compared with the liquid phase process.

[0011]There are many examples which obtain the ultrafine particle of titanium oxide by a gaseous phase method, for example, in JP,6-340423,A. In the method of hydrolyzing titanium tetrachloride in a flame and manufacturing titanium oxide, adjust the mole ratio of oxygen, titanium tetrachloride, and hydrogen, it is made to react, and the method of obtaining titanium oxide with high rutile content is indicated. By making titanium tetrachloride hydrolyze into JP,7-316536,A in the elevated-temperature gaseous phase, and cooling a resultant quickly, In the method of manufacturing crystalline-titanium-oxide powder, the way the first [ an average of ] particle diameter obtains crystalline substance transparent titanium oxide (not less than 40 nm and 150 nm or less) is indicated by specifying flame temperature and the titanium concentration in material gas. However, in any case, it is particles, but only titanium oxide with high rutile content is obtained, and it is not suitable for using it as a photocatalyst use and a solar cell use.

[0012]The manufacturing method which adjusts the content ratio of rutile because the way anatase manufactures titanium oxide of a main phase by a gaseous phase method changes the ratio of hydrogen in the gaseous mixture of oxygen and hydrogen into JP,3-252315,A in gaseous phase reaction, for example is indicated.

Titanium oxide whose rutile content is 9% is indicated.

However, the particle diameter of the illustrated titanium oxide is 0.5–0.6 micrometer, and is coarser than the range of the particle diameter generally called ultrafine particle.

[0013] If titanium oxide is manufactured by the gaseous phase method which uses halogenation titanium as a raw material, it will be easy to obtain an ultrafine particle, but since halogen of raw material origin remains in titanium oxide, the dehalogenation by heating or rinsing is needed in many cases. However, sintering of particles advances with heating for low halogenation, and specific surface area falls easily, and also transition of the crystal form to a rutile type [ type / anatase ] may produce ultrafine particle titanium oxide. In order to control the fall of specific surface area, and crystal transition, heating of low temperature or a short time must be performed, but it stops fully being able to carry out dehalogenation. The low chlorinating method of ultrafine particle titanium oxide is indicated by JP,10-251021,A, for example. This method is the method of making a steam contact, rolling titanium oxide all over a cylindrical shape revolving heating furnace, and making a chlorine content low. The rutile content of the titanium oxide indicated to this was as high as 15%.

[0014] On the other hand, although the halogen which remained in the titanium oxide particle surface could be removed in the dehalogenation by rinsing etc., since halogen inside particles was not able to contact water easily, it had the problem that internal halogen remained easily.

[0015] These ultrafine particle titanium oxide of the low rutile type whose halogen content is [ like ] low in the conventional gaseous phase method was not obtained.

[Patent documents 1] JP,10-255863,A [Patent documents 2] JP,2000-340269,A [Patent documents 3] JP,6-340423,A [Patent documents 4] JP,7-316536,A [Patent documents 5] JP,10-251021,A

[Nonpatent literature 1] "Optical clean revolution" Akira Fujishima, Kazuhito Hashimoto, Toshiya Watabe collaboration, CMC Co., Ltd., 143 – 145 pages (1997)

[Nonpatent literature 2] "Everything about titanium oxide photocatalysts" (Kazuhito Hashimoto and Fujishima Showa edit, CMC Co., Ltd., 29 – 30 pages (1998))

[Nonpatent literature 3] M.Graezel, Nature, 353, 737, (1991)

[Nonpatent literature 4] "Titanium oxide" Seino \*\*\*\*, Gihodo Shuppan Co., Ltd., Inc., p.129 (1991),

[Nonpatent literature 5] ("Ultrafine particle handbook" Saito [ Susumu ] 6 editorial supervision, a FUJI techno system, 388 pages (1990))

[0016]

[Problem(s) to be Solved by the Invention] This invention is made that the above-mentioned problem should be solved, and there is a technical problem of this invention in excelling in dispersibility and providing ultrafine particle titanium oxide of a low rutile type with a low halogen content, and a manufacturing method for the same in a gaseous phase method.

[0017]

[Means for Solving the Problem] As a result of inquiring wholeheartedly in view of an aforementioned problem, this invention persons find out that it excels in dispersibility and ultrafine particle titanium oxide of a low rutile type with a low halogen content can be manufactured in a gaseous phase method, and came to solve an aforementioned problem.

[0018] In a gaseous phase method to which gas and a oxidizing gas (mixed gas containing oxygen, a steam, or these) with which this invention contains halogenation titanium are made to react, . After making this material gas react, controlling cooking temperature and cooking time, are obtained by carrying out dehalogenation. Ultrafine particle titanium oxide of a low rutile type which rutile content is 5% or less of titanium oxide, and has a high BET specific surface area and the specific characteristic, and a manufacturing method for the same are provided.

[0019] That is, this invention includes the following inventions.

(1) Are titanium oxide obtained by making gas and a oxidizing gas containing halogenation titanium react, and rutile content at 5% or less. And when  $B$  ( $m^2/g$ ) and a total halogen content of titanium oxide are set to  $C$  (mass ppm) for specific surface area of titanium oxide measured with a BET one point method for BET method, Titanium oxide when it is shown by  $C \leq 650e^{0.02B}$  and is considered as aqueous suspension of 1 mass %, wherein halogen more than 80 mass % of the amount of halogen contained in titanium oxide after neglect for 30 minutes at 20 \*\* shifts the aqueous suspension to the liquid phase.

(2) Titanium oxide given in the above (1) in which halogen more than 90 mass % of the amount of halogen contained in titanium oxide shifts to the liquid phase.

(3) Titanium oxide the above (1) in which titanium oxide contains each element of Fe, aluminum, Si,

and S below 100 mass ppm, respectively, or given in (2).

(4) Titanium oxide given in above-mentioned (1) – (3) in which titanium oxide has the specific surface area of  $10\text{--}200\text{--m}^2/\text{g}$ .

(5) Titanium oxide given in any 1 paragraph of above-mentioned (1) – (4) whose main phase of titanium oxide is anatase.

(6) Titanium oxide given in the above (5) whose anatase content of titanium oxide is not less than 90%.

(7) Titanium oxide given in any 1 paragraph of above-mentioned (1) – (4) whose main phase of titanium oxide is brookite.

(8) Titanium oxide of the above (7) whose brookite content of titanium oxide is not less than 90%.

(9) Titanium oxide given in any 1 paragraph of above-mentioned (1) – (8) in which titanium oxide has a diameter of 90% accumulation mass particle size distribution of 2.5 micrometers or less measured with a laser diffraction type grading analysis meter.

(10) Titanium oxide given in any 1 paragraph of above-mentioned (1) – (9) said whose halogenation titanium is titanium tetrachloride and in which said halogen is chlorine.

(11) In the gaseous phase method for manufacturing titanium oxide by making gas and a oxidizing gas containing halogenation titanium react, A manufacturing method of titanium oxide in which temperature in this reactor is characterized by not less than 800 \*\* being less than 1,100 \*\* when gas and a oxidizing gas containing halogenation titanium are introduced into a reactor, respectively and are made to react.

(12) A manufacturing method of titanium oxide given in the above (11) whose with a not less than 800 \*\* [ temperature below 1,100 \*\* ] holding time gas and a oxidizing gas containing halogenation titanium is 0.1 or less second within a reactor.

(13) A manufacturing method of titanium oxide the above (11) which gas and a oxidizing gas containing halogenation titanium are preheated by not less than 600 \*\* and less than 1,100 \*\*, respectively, and is introduced into a reactor, or given in (12).

(14) a reaction -- halogenation -- titanium -- one -- mol -- receiving -- inactive gas -- 0.1 – 20 -- mol -- a rate -- having mixed -- material gas -- halogenation -- titanium -- one -- mol -- receiving -- one – 30 -- mol -- a oxidizing gas -- carrying out -- having -- the above -- ( -- 11 -- ) – ( -- 13 -- ) -- some -- one -- a paragraph -- a statement -- titanium oxide -- a manufacturing method .

(15) A manufacturing method of titanium oxide given in any 1 paragraph of above-mentioned (11) – (14), wherein a oxidizing gas is oxygen gas containing a steam.

(16) A manufacturing method of titanium oxide given in the above (15) in which a oxidizing gas contains 0.1 mol or more of steams to 1 mol of oxygen gas.

(17) A manufacturing method of titanium oxide given in any 1 paragraph of above-mentioned (11) – (16) in which said halogenation titanium is titanium tetrachloride.

(18) The above (11) Manufacturing method of titanium oxide removing halogen for titanium oxide manufactured with a manufacturing method given in any 1 paragraph of – (17) by dry type.

(19) A manufacturing method of titanium oxide given in the above (18) whose method of removing halogen by dry type is the method of performing by heating titanium oxide at 200–500 \*\*.

(20) A manufacturing method of titanium oxide given in the above (18) whose method of removing halogen by dry type is the method of performing while heating gas containing a steam at 200–1000 \*\* and making titanium oxide contact.

(21) A manufacturing method of titanium oxide given in the above (20) which is the air in which gas containing a steam contains a steam in more than 0.1 capacity %.

(22) A manufacturing method of titanium oxide given in the above (20) whose steam is 0.01 or more in a mass ratio to titanium oxide.

(23) The above (11) Manufacturing method of titanium oxide obtaining a slurry which removes halogen for titanium oxide manufactured with a manufacturing method given in any 1 paragraph of – (17) by a wet type, and contains titanium oxide.

(24) A manufacturing method of titanium oxide given in the above (23) which is the method of separating halogen in which a method of removing halogen by a wet type made titanium oxide suspended in water, and shifted to the liquid phase out of a system.

(25) A manufacturing method of titanium oxide the above (23) whose method of removing halogen by a wet type is a method of separating halogen by ultrafiltration membrane, or given in (24).

(26) A manufacturing method of titanium oxide the above (23) whose method of removing halogen by



a wet type is a method of separating halogen by a reverse osmotic membrane, or given in (24).

(27) A manufacturing method of titanium oxide the above (23) whose method of removing halogen by a wet type is a way the filter press separates halogen, or given in (24).

(28) The above (11) Granular material by which titanium oxide manufactured with a manufacturing method of a statement being included in any 1 paragraph of - (27).

(29) The above (11) Slurry by which titanium oxide manufactured with a manufacturing method of a statement being included in any 1 paragraph of - (27).

(30) The above (11) Constituent by which titanium oxide manufactured with a manufacturing method of a statement being included in any 1 paragraph of - (27).

(31) The above (11) Photocatalyst material by which titanium oxide manufactured with a manufacturing method of a statement being included in any 1 paragraph of - (27).

(32) The above (11) Charge of wet solar cell material by which titanium oxide manufactured with a manufacturing method of a statement being included in any 1 paragraph of - (27).

(33) The above (11) Dielectric raw material by which titanium oxide manufactured with a manufacturing method of a statement being included in any 1 paragraph of - (27).

(34) The above (11) Silicone rubber additive agent by which titanium oxide manufactured with a manufacturing method of a statement being included in any 1 paragraph of - (27).

Specific surface area which rutile content measured with a BET one point method for BET method 5% or less (35)  $10\text{--}200\text{m}^2/\text{g}$ , A diameter of 90% accumulation mass particle size distribution measured with a laser diffraction type grading analysis meter is a titanium oxide particle of 2.5 micrometers or less, And when a halogen content inside B ( $\text{m}^2/\text{g}$ ) and a titanium oxide particle is made into  $C_i$  (mass ppm) for specific surface area of titanium oxide measured with a BET one point method for BET method, A titanium oxide particle, wherein the amount of halogen contained in an inside of particles is shown by  $0 \leq C_i \leq 650k e^{0.02B}$  (k is 0.20).

(36) A titanium oxide particle given in the above (35) which contains in an inside of particles halogen of quantity shown by  $10 < C_i \leq 650k e^{0.02B}$  (k is 0.15).

[0020]

[Embodiment of the Invention]As halogenation titanium which is a raw material of titanium oxide of this invention, the titanium chloride which is easy to come to hand industrially, especially titanium tetrachloride are preferred. Therefore, although the case where halogen is chlorine about this invention is hereafter explained as an example of representation, this invention can be applied also when halogen is bromine or iodine. In spite of manufacturing low rutile type ultrafine particle titanium oxide of this invention using titanium tetrachloride by a gaseous phase method, chlorine hardly exists in the inside of particles. Although the chlorine which remains inside particles is temporally diffused from the inside of a particle to the surface, it may corrode and a substrate may be deteriorated, in easy dechlorination of rinsing, desiccation, etc., it is hard to remove. Therefore, it is desirable for chlorine not to exist in the inside of a titanium oxide particle. About the chlorine content inside the particles occupied to the inside of the sum total chlorinity inside a particle surface and particles, the ratio of the chlorine (water extraction chlorine is called) extracted from titanium oxide with pure water and all the chlorine (all the chlorine is called) contained in a titanium oxide particle is made into an index, and it is a lower type (1).

$R = \text{WCL} / \text{TCL} \times 100 \dots\dots\dots(1)$

(R expresses the rate of surface chlorine (%) among a formula, WCL expresses the content (mass %) of the water extraction chlorine contained in titanium oxide, and TCL expresses the content (mass %) of all the chlorine contained in titanium oxide.) -- it is shown that there is so little chlorine content inside a titanium oxide particle that the value of R expressed is high. About titanium oxide in this invention, it is desirable still more preferred that R is not less than 80%, and it is not less than 90%.

[0021]The ultrafine particle titanium oxide obtained by the gaseous phase method which uses titanium tetrachloride of this invention as a raw material is rutile content.[The peak height corresponding to a rutile type crystal [ in / in rutile content / an X diffraction ] (it carries out abbreviated to Hr.), The ratio computed from the peak height (it carries out abbreviated to Hb.) corresponding to a brookite type crystal, and the peak height (it carries out abbreviated to Ha.) corresponding to an anatase type crystal (=  $100 \times \text{Hr} / (\text{Hr} + \text{Ha} + \text{Hb})$  is said.) ] is 5% or less of ultrafine particle titanium oxide (it may be hereafter called for short ultrafine particle titanium oxide of a low



rutile type.), and it is following general formula (2):  $C \leq 650 \times e^{0.02B}$  also before a dechlorination step not only depending on after a dechlorination step but depending on the case. ....(2)

It comes out and has a total chlorine content expressed. C shows a total chlorine content (mass %) among a formula. C measures the liquid which added fluoric acid solution to titanium oxide, and carried out heating and dissolving to it with microwave, for example with the potentiometric titration by silver nitrate, obtains the mass of chlorine in titanium oxide, and is obtained by  $\frac{C}{m}$  with the mass of titanium oxide using this. B expresses a BET specific surface area ( $m^2/g$ ), and the range is  $10-200 m^2/g$ . It has the characteristic of being expressed.

[0022] That is, ultrafine particle titanium oxide of a low rutile type of this invention is titanium oxide with few total chlorine contents with which it is satisfied of the conditions of the above-mentioned general formula (2) in drawing 1, and R of the above-mentioned formula (1) is a titanium oxide particle with small chlorine content inside large particles. Ultrafine particle titanium oxide by the gaseous phase method which uses conventional titanium tetrachloride as a raw material, Even if it is a low rutile type titanium dioxide, it is what has the characteristic of the field plotted by the upper part of the curve expressed with  $C = 650 \times e^{0.02B}$  shown in drawing 1 in the relation between a BET specific surface area and a total chlorine content. It was a titanium oxide particle whose chlorine content inside the above-mentioned particles is also large further again. In particular, the dechlorination of the titanium oxide with larger specific surface area is hard to be carried out, and it has a tendency which a chlorine content increases exponentially.

[0023] As for the low rutile type titanium dioxide of this invention, the relation between a chlorine content and a BET specific surface area satisfies the characteristic of a general formula (2), it is an ultrafine particle -- usually -- the range of a BET specific surface area --  $10-200 m^2/g$  -- they are  $40-200 m^2/g$  and a thing which has the range of  $45-120 m^2/g$  still more preferably.

[0024] ultrafine particle titanium oxide of a low rutile type of this invention -- the content of Fe, aluminum, Si, and S -- below 100 mass each ppm -- desirable -- each 0.1 to 100 mass ppm -- more -- desirable -- each 0.1 to 50 mass ppm -- it is each 0.1 to 10 mass ppm still more preferably. In order for such impurity concentration to be less than 0.1 ppm, raw material which manufactures titanium oxide is made into a high grade, and it is necessary in equipment construction material to use a corrosion-resistant high thing more etc. It is economically more advantageous for titanium oxide of this invention not to carry out each impurity less than 0.1 mass ppm in the use usually used.

[0025] The low rutile type titanium dioxide of this invention is characterized by dispersibility being high. In this invention, the laser diffraction type particle-size-distribution measuring method was adopted as an index of dispersibility, and particle size distribution was measured. According to "ultrafine particle handbook" Saito [ Susumu ] 6 editorial supervision, a FUJI techno system, p93, and (1990), there are a sedimentation method, a microscopic method, light scattering measurement, a direct count method, etc. in the measuring method of dispersibility, but. Among these, a sedimentation method and a direct count method are not less than hundreds of nm, and their measurable particle diameter is unsuitable for measuring the dispersibility of an ultrafine particle. Since measured value is changed by the sampling of an object sample, or pretreatment of a sample, a microscopic method cannot be said as a desirable measuring method, either. On the other hand, light scattering measurement can measure particle diameter in several nanometers -- several micrometers, and are suitable for measurement of the ultrafine particle. The measurement procedure of particle size distribution is explained below.

[0026] Ultrasonic irradiation (46 kHz, 65W) is carried out to the slurry which added 50 ml of pure water, and 10% sodium hexametaphosphate solution 100mul to the titanium oxide 0.05g for 3 minutes. Particle size distribution is measured applying this slurry to a laser diffraction type size distribution measuring device (Shimadzu Corp. make SALD-2000J). Thus, if the value of the diameter of 90% accumulation mass particle size distribution in the measured particle size distribution (it may be hereafter written as D90) is small, it will be judged that good dispersibility is shown to a hydrophilic solvent. Although it is also possible to make the diameter of accumulation mass particle size distribution into the index of dispersibility 50%, it is hard to detect the bad floc of dispersibility, and is not desirable. As for ultrafine particle titanium oxide of this invention, it is preferred that D90 is 2.5 micrometers or less.

[0027] Finely divided titanium oxide of this invention is contained as a particle component using the raw material, paints, or photocatalyst effect of various constituents, for example, can be used as the

raw material of various products, such as cosmetics, an ultraviolet-rays shielding material, a dielectric or silicone rubber, and a solar cell, and an additive agent.

[0028]Next, a manufacturing method is explained. The manufacturing method of common titanium oxide by a gaseous phase method is publicly known, and if titanium tetrachloride is oxidized under about 1,000 °C reaction condition using oxidizing gases, such as oxygen or a steam, particulate titanium oxide will be obtained.

[0029]In order to obtain titanium oxide of an ultrafine particle in a gaseous phase method, growth time (growth zone) of particles must be shortened. That is, the grain growth by sintering etc. can be stopped by performing cooling, dilution, etc. promptly after a reaction and shortening elevated-temperature holding time as much as possible. It leads also to shortening of elevated-temperature holding time controlling the heat rearrangement to rutile from anatase, and particles with high anatase content can be obtained.

[0030]In the titanium oxide generally obtained by the gaseous phase method which uses titanium tetrachloride as a raw material, chlorine of 0.1 – 2 mass % usually remains. The chlorine content to which the point which can combine chlorine etc. remains in a titanium oxide particle surface when those (the above-mentioned Seino et al. "titanium oxide") with  $13\text{-piece } [\text{nm}]^{-2}$  and all these joints are chlorinating is theoretically expressed in the anatase-type-titanium-oxide surface by the lower type (3).

$$Y=0.077 \times A \quad (3)$$

(Y shows among a formula the chlorine content (mass %) which remains in a titanium oxide particle surface, and A shows specific surface area ( $\text{m}^2/\text{g}$ ).)

For example, according to said formula (3), the chlorine content which remains in the titanium oxide particle surface which has the specific surface area of  $100\text{-m}^2/\text{g}$  becomes about 8 mass %.

[0031]In practice, that chlorine and a oxidizing gas replace at a reaction, and when chlorine carries out balanced movement according to the level-of-chlorine difference of a titanium oxide particle surface and the gaseous phase, the chlorine content of titanium oxide may become low a little rather than the value obtained by said formula (3), but. It is considered that shortening of the elevated-temperature holding time in a reaction does not complete oxidation reaction of titanium tetrachloride, and makes the titanium oxide in which a part is chlorinated increased. Since residual chlorine also becomes increasing the chlorinity inside the grain child left behind inside a titanium oxide particle, the heat-treatment which chlorine removal takes will turn an elevated temperature and for a long time, and will produce the fall of specific surface area. Therefore, although a chlorine content is high [ the ultrafine particle conventionally obtained by a gaseous phase method / of what has high anatase content ], or low, it is said that anatase content is low.

[0032]In the gaseous phase method for manufacturing titanium oxide by reacting the gas and the oxidizing gas containing titanium tetrachloride in this invention (high temperature oxidation), The oxidizing gas heated at the gas containing the titanium tetrachloride heated at not less than 600 °C less than 1,100 °C and not less than 600 °C less than 1,100 °C is supplied to a coil, respectively, By making the titanium oxide produced by making react stagnate in the time for 0.1 or less second, and a coil on the not less than 800 °C high temperature conditions below 1,100 °C, In the relation between a BET specific surface area and a chlorine content, low rutile type ultrafine particle titanium oxide with low total chlorine content, especially chlorine content inside particles is obtained, It found out that low rutile type ultrafine particle titanium oxide also with a low chlorine content inside particles whose total chlorine content is still lower was obtained by dechlorinating this. Here, there are a dry method and wet process in a dechlorination. A dry type dechlorination method heats titanium oxide using heating apparatus, such as a cylindrical shape revolving heating furnace, a hot wind circle method heating furnace, a fluidized-drying furnace, and a churning drying furnace, and has a method of removing chlorine, for example. This invention is not necessarily limited to these heating apparatus. A wet dechlorination method makes titanium oxide suspended to pure water, and has a method of separating the chlorine which shifted to the liquid phase out of a system, for example. After separating chlorine out of a system, the obtained titanium oxide may be dried.

[0033]Not less than 800 °C less than 1,100 °C is desirable still more preferred, and the temperature in the coil which introduces titanium tetrachloride content gas or a oxidizing gas is not less than 900 °C less than 1,000 °C. By making the degree of coil internal temperature high, simultaneously with mixing, since it completes, uniform karyogenesis is increased, and the reaction can make a reaction

(CVD) zone small. If the degree of coil internal temperature is lower than 800 \*\*, although titanium oxide with high anatase content will be easy to be obtained, a reaction is insufficient and chlorine remains inside a titanium oxide particle. If the degree of coil internal temperature will be not less than 1,100 \*\*, rutile transition and particle growth will advance and a low rutile type and an ultrafine particle will not be obtained.

[0034] Since this reaction is an exoergic reaction on the other hand when material gas is introduced into a coil and a reaction advances, the reaction zones where reaction temperature exceeds 1,100 \*\* exist. Although there is some device heat dissipation, unless it quenches, a titanium oxide particle will grow rapidly and a crystal form will transfer it to rutile. Then, in this invention, not less than 800 \*\* elevated-temperature holding time below 1,100 \*\* is especially made into the range for 0.01 to 0.05 second preferably for 0.005 to 0.1 second 0.1 or less second. If elevated-temperature holding time exceeds 0.1 second, since transition to rutile and sintering of particles will advance, it is not desirable. Since elevated-temperature holding time becomes short [ the oxidation reaction time of titanium tetrachloride ] in less than 0.005 second, it is necessary to carry out under the conditions which are easy to perform oxidation, such as using the amount of oxygen superfluous enough compared with titanium tetrachloride. If oxidation is insufficient, it leads to the increase in residual chlorinity inside particles.

[0035] As a means of quenching, the method of introducing gas, such as a lot of cooling air and nitrogen, into a reaction mixture, for example or the method of spraying water is adopted.

[0036] Rutile transition and grain growth can be controlled by being able to obtain an ultrafine particle with a low chlorine content inside particles by controlling the temperature in a coil at said not less than 800 \*\* less than 1,100 \*\*, and controlling elevated-temperature holding time at 0.1 or less second.

[0037] In order for the temperature in a coil to be said not less than 800 \*\* less than 1,100 \*\*, it is preferred to adjust the cooking temperature of material gas to not less than 600 \*\* 1,100 \*\* or less. Although the heated material gas reacts and generates heat within a coil, the temperature in a coil cannot be not less than 800 \*\* easily for material gas temperature to be less than 600 \*\*. Although there is device heat dissipation that material gas temperature is not less than 1,100 \*\*, the temperature in a coil becomes easy to exceed 1,100 \*\*.

[0038] It is desirable still more preferred that it is 0.1–20 mol of inactive gas to 1 mol of gaseous titanium tetrachlorides, and the material gas presentation containing titanium tetrachloride is 4–20 mol. When there is less inactive gas than said range, the titanium oxide particle density in reaction zones increases, and since it condenses and becomes easy to sinter, ultrafine particle titanium oxide is hard to be obtained. When there is more inactive gas than said range, reactivity falls and the recovery rate as titanium oxide falls.

[0039] As for the amount of oxygen gas made to react to the material gas containing titanium tetrachloride, it is preferred that it is 1–30 mol to 1 mol of titanium tetrachloride. It is 5–30 mol still more preferably. If the amount of oxygen gas is increased, an ultrafine particle will become the number of karyogenesis increases and is easy to be obtained; but even if it exceeds 30 mol, most effects of making the number of karyogenesis increasing cannot be found. Even if the amount of oxygen gas exceeds 30 mol, it is uninfluential in the characteristic of titanium oxide, but a maximum is set up from an economical viewpoint. On the other hand, if the amounts of oxygen gas run short to titanium tetrachloride, it will be titanium oxide with many oxygen deficiencies, and will color. The steam other than oxygen may be contained in the oxidizing gas. Although each gas which mixed inactive gas (nitrogen, argon, etc.) can use it for oxygen, oxygen containing a steam, air, and these oxidizing gases, for example, since reaction temperature tends to control a oxidizing gas, its oxygen containing a steam is preferred.

[0040] As for the dechlorination by heating of titanium oxide, it is preferred to carry out with the not less than 200 \*\* cooking temperature at 500 \*\* or less, contacting a steam to titanium oxide powder so that the mass ratio (the mass/titanium oxide of = steam are the same as that of mass and the following) of water and titanium oxide may become 0.01 or more. Preferably, the mass ratio of water and titanium oxide is 0.04 or more, and cooking temperature is not less than 250 \*\* 450 \*\* or less. If cooking temperature exceeds 500 \*\*, sintering of a titanium oxide particle will progress and grain growth will arise. If cooking temperature is less than 200 \*\*, the efficiency of a dechlorination will fall extremely. A dechlorination runs and goes, when chlorine on the surface of titanium oxide carries out a substitution reaction to the water near the particle, or the adjoining surface-water-of-aggregate

acid radical of particles. When chlorine of a titanium oxide particle surface is replaced by water, it is dechlorinated, without carrying out grain growth, but when replaced by the surface-water-of-aggregate acid radical of the adjoining particles, grain growth will be carried out simultaneously with a dechlorination. Since the probability which carries out a substitution reaction to the particle surface hydroxyl group in which it adjoins as titanium oxide especially with large specific surface area becomes high, it is easy to carry out grain growth. That is, in order to attain dechlorination, controlling grain growth, the mass ratio of water and titanium oxide is also important, and if the mass ratio of water and titanium oxide is 0.01 or more, the effect which controls grain growth will be accepted.

[0041]As for the steam contacted to titanium oxide, it is preferred to use it, mixing with the gas which has a role which moves efficiently the chlorine separated from titanium oxide out of a system. As such gas, air is mentioned, for example. When using air, as for a steam, it is desirable still more preferred that more than 0.1 capacity % is contained in air, and more than 5 capacity % is more than 10 capacity % especially preferably. As for the air having contained the steam, it is preferred to heat at not less than 200 °C or less.

[0042]Since chlorine hardly exists in the inside of particles, low rutile type ultrafine particle titanium oxide by this invention can also form low-salt base by a wet type. Titanium oxide is made suspended to pure water, and the way ultrafiltration membrane, a reverse osmotic membrane, the filter press, etc. separate the chlorine which shifted to the liquid phase out of a system is mentioned to the wet dechlorination method, for example. Thus, low rutile type ultrafine particle titanium oxide with a total halogen content and the halogen content inside particles low in the relation of the BET specific surface area of this invention and halogen content which are manufactured, By carrying out dehalogenation of the halogen of a particle surface more nearly thoroughly preferably, low rutile type ultrafine particle titanium oxide whose total halogen content is very low can be obtained in a relation with a BET specific surface area. Therefore, low rutile type ultrafine particle titanium oxide of this invention, The specific surface area which rutile content measured with the BET one point method for BET method 5% or less like the above 10–200m<sup>2</sup>/g, The diameter of 90% accumulation mass particle size distribution measured with a laser diffraction type grading analysis meter is a titanium oxide particle of 2.5 micrometers or less, And when the halogen content inside B (m<sup>2</sup>/g) and a titanium oxide particle is made into C<sub>i</sub> (mass ppm) for the specific surface area of the titanium oxide measured with the BET one point method for BET method, The amount of halogen contained in the inside of particles  $0 < C_i \leq 650k e^{0.02B}$  (k is 0.20), It is preferably characterized by  $0 < C_i \leq 650k e^{0.02B}$  (k is 0.20) and the thing more preferably shown by  $10 < C_i \leq 650k e^{0.02B}$  (k is 0.15).

[0043]

[Example]Although an example and a comparative example explain concretely hereafter, this invention is not limited to these at all.

[0044]Example 1:11.8Nm<sup>3</sup>/hr (N means a normal condition.) It is below the same. The titanium tetrachloride dilution gas which diluted gaseous titanium tetrachloride with the nitrogen gas of 8–Nm<sup>3</sup>/hr is preheated at 900 °C, The oxidizing gas which mixed oxygen of 8–Nm<sup>3</sup>/hr and a 32–Nm<sup>3</sup>/hr steam was preheated at 800 °C, and these material gas was introduced into the reactor made from silica glass. As it had been 0.1 second about the not less than 800 °C elevated-temperature holding time below 1,100 °C, finely-divided-titanium-oxide powder was caught with the bag filter made from polytetrafluoroethylene after introducing cooling air into a coil.

[0045]The dechlorination of the obtained titanium oxide was carried out to the cylindrical shape revolving heating furnace with the mass ratio 0.02 of through, water, and titanium oxide, and the cooking temperature at 450 °C. Then, the water extraction chlorine content was [ the BET specific surface area / 900 mass ppm and the total chlorine content of the obtained titanium oxide of 22m<sup>2</sup>/g and a rutile content ratio (it is also called rutile content.) ] 1,000 mass ppm 1%. However, a BET specific surface area is measured with the Shimadzu surface area measuring instrument (models are flow SOBU II and 2300), The peak height corresponding to a rutile type crystal [ in / in a rutile content ratio / an X diffraction ] (it carries out abbreviated to Hr.), It is the ratio (=100xHr/(Hr+Ha+Hb)) computed from the peak height (it carries out abbreviated to Hb.) corresponding to a brookite type crystal, and the peak height (it carries out abbreviated to Ha.) corresponding to an anatase type crystal. It is a water extraction chlorine content to a formula (1). 900 mass ppm, total

chlorine content The rate of surface chlorine computed by substituting 1,000 mass ppm was higher than 80%, and the total chlorine content showed the numerical value smaller than the value computed by substituting specific surface area  $^2$ [ of 22 m ]/g for a formula (2).

[0046]It was 1.1 micrometers as a result of measuring the diameter D90 of accumulation mass particle size distribution 90% by a laser diffraction type particle-size-distribution measuring method about the particle size distribution of the titanium oxide powder obtained here. The rate of rutile-izing, a BET specific surface area, a total chlorine content, the rate of surface chlorine, D90 and Fe, aluminum, Si, and the analysis result of S are shown in Table 1.

[0047]The titanium tetrachloride dilution gas which diluted gaseous titanium tetrachloride of example 2:5.9Nm<sup>3</sup>/hr with the nitrogen gas of 30-Nm<sup>3</sup>/hr is preheated at 1,000 \*\*, The oxidizing gas which mixed oxygen of 4-Nm<sup>3</sup>/hr and the steam of 16-Nm<sup>3</sup>/hr was preheated at 1,000 \*\*, and these material gas was introduced into the reactor made from silica glass. As it had been 0.03 second about the not less than 800 \*\* elevated-temperature holding time below 1,100 \*\*, finely-divided-titanium-oxide powder was caught with the bag filter made from polytetrafluoroethylene after introducing cooling air into a coil.

[0048]The obtained titanium oxide was put into the hot wind circulation heating furnace, and the dechlorination was carried out to water with the titanium oxide mass ratio 0.04 and the cooking temperature at 450 \*\*. In this way, the water extraction chlorine content was [ the BET specific surface area / 900 mass ppm and the total chlorine content of the obtained titanium oxide of 65m<sup>2</sup>/g and rutile content ] 1,100 mass ppm 3%. It is a water extraction chlorine content to a formula (1). 900 mass ppm, total chlorine content The rate of surface chlorine computed by substituting 1,100 mass ppm was higher than 80%, and the total chlorine content showed the numerical value smaller than the value computed by substituting specific surface area  $^2$ [ of 65 m ]/g for a formula (2). The diameter D90 of 90% accumulation mass particle size distribution in the particle size distribution measured by the laser diffraction type particle-size-distribution measuring method of this powder was 1.9 micrometers. The rate of rutile-izing, a BET specific surface area, a total chlorine content, the rate of surface chlorine, D90 and Fe, aluminum, Si, and the analysis result of S are shown in Table 1.

[0049]The titanium tetrachloride dilution gas which diluted gaseous titanium tetrachloride of example 3:4.7Nm<sup>3</sup>/hr with the nitrogen gas of 36-Nm<sup>3</sup>/hr is preheated at 1,000 \*\*, The oxidizing gas which mixed the air of 36-Nm<sup>3</sup>/hr and the steam of 25-Nm<sup>3</sup>/hr was preheated at 1,000 \*\*, and these material gas was introduced into the reactor made from silica glass. As it had been 0.02 second about the not less than 800 \*\* elevated-temperature holding time below 1,100 \*\*, finely-divided-titanium-oxide powder was caught with the bag filter made from polytetrafluoroethylene after introducing cooling air into a coil.

[0050]The obtained titanium oxide was put into the hot wind circulation heating furnace, and the dechlorination was carried out to water with the titanium oxide mass ratio 0.06 and the cooking temperature at 350 \*\*. In this way, water extraction chlorine content was [ the BET specific surface area / 1,800 mass ppm and the total chlorine content of the obtained titanium oxide of 97m<sup>2</sup>/g and rutile content ] 2,000 mass ppm 1%. It is a water extraction chlorine content to a formula (1). 1,800 mass ppm, total chlorine content The rate of surface chlorine computed by substituting 2,000 mass ppm was higher than 80%, and total chlorine content showed the numerical value smaller than the value computed by substituting specific surface area  $^2$ [ of 97 m ]/g for a formula (2). The diameter D90 of 90% accumulation mass particle size distribution in the particle size distribution measured by the laser diffraction type particle-size-distribution measuring method of this powder was 2.2 micrometers. The rate of rutile-izing, a BET specific surface area, a total chlorine content, the rate of surface chlorine, D90 and Fe, aluminum, Si, and the analysis result of S are shown in Table 1.

[0051]The titanium tetrachloride dilution gas which diluted gaseous titanium tetrachloride of comparative example 1:11.8Nm<sup>3</sup>/hr with the nitrogen gas of 8-Nm<sup>3</sup>/hr is preheated at 900 \*\*, The oxidizing gas which mixed oxygen of 8-Nm<sup>3</sup>/hr and a 32-Nm<sup>3</sup>/hr steam was preheated at 800 \*\*, and these material gas was introduced into the reactor made from silica glass. As it had been 0.2 second about the not less than 800 \*\* elevated-temperature holding time below 1,100 \*\*, finely-divided-titanium-oxide powder was caught with the bag filter made from polytetrafluoroethylene after introducing cooling air into a coil.

[0052]The dechlorination of the obtained titanium oxide was carried out to through and water in the

cylindrical shape revolving heating furnace with the titanium oxide mass ratio 0.02 and the cooking temperature at 450 \*\*. In this way, the water extraction chlorine content was [ the BET specific surface area / 300 mass ppm and the total chlorine content of the obtained titanium oxide of  $19\text{m}^2/\text{g}$  and a rutile content ratio ] 300 mass ppm 11%. It is water extraction chlorine content to a formula (1). 300 mass ppm, total chlorine content The rate of surface chlorine computed by substituting 300 mass ppm was higher than 80%, and total chlorine content showed the numerical value smaller than the value computed by substituting specific surface area  $^2$ [ of  $19\text{ m}^2/\text{g}$  for a formula (2). The diameter D90 of 90% accumulation mass particle size distribution in the particle size distribution measured by the laser diffraction type particle-size-distribution measuring method of this powder was 0.8 micrometer. The rate of rutile-izing, a BET specific surface area, a total chlorine content, the rate of surface chlorine, D90 and Fe, aluminum, Si, and the analysis result of S are shown in Table 1. [0053]The titanium tetrachloride dilution gas which diluted gaseous titanium tetrachloride of comparative example 2:  $4.7\text{Nm}^3/\text{hr}$  with the nitrogen gas of  $36\text{-Nm}^3/\text{hr}$  is preheated at 800 \*\*, The oxidizing gas which mixed the air of  $36\text{-Nm}^3/\text{hr}$  and the steam of  $25\text{-Nm}^3/\text{hr}$  was preheated at 800 \*\*, and these material gas was introduced into the reactor made from silica glass. This coil temperature was controlled at 750 \*\*, and finely-divided-titanium-oxide powder was caught with the bag filter made from polytetrafluoroethylene after introducing cooling air into a coil so that material gas might be stagnated for 0.08 second.

[0054]The obtained titanium oxide was put into the hot wind circulation heating furnace, and the dechlorination was carried out to water with the titanium oxide mass ratio 0.04 and the cooking temperature at 350 \*\*. In this way, water extraction chlorine content was [ the BET specific surface area / 2,800 mass ppm and the total chlorine content of the obtained titanium oxide of  $74\text{m}^2/\text{g}$  and rutile content ] 3,900 mass ppm 2%. It is a water extraction chlorine content to a formula (1). 2,800 mass ppm, total chlorine content The rate of surface chlorine computed by substituting 3,900 mass ppm was lower than 80%, and total chlorine content showed the bigger numerical value than the value computed by substituting specific surface area  $^2$ [ of  $74\text{ m}^2/\text{g}$  for a formula (2). The diameter D90 of 90% accumulation mass particle size distribution in the particle size distribution measured by the laser diffraction type particle-size-distribution measuring method of this powder was 3.6 micrometers. The rate of rutile-izing, a BET specific surface area, a total chlorine content, the rate of surface chlorine, D90 and Fe, aluminum, Si, and the analysis result of S are shown in Table 1.

[0055]The titanium tetrachloride dilution gas which diluted gaseous titanium tetrachloride of comparative example 3:  $5.9\text{Nm}^3/\text{hr}$  with the nitrogen gas of  $30\text{-Nm}^3/\text{hr}$  is preheated at 1,100 \*\*, The oxidizing gas which mixed oxygen of  $4\text{-Nm}^3/\text{hr}$  and the steam of  $16\text{-Nm}^3/\text{hr}$  was preheated at 1,100 \*\*, and these material gas was introduced into the reactor made from silica glass. This coil temperature was controlled at 1,200 \*\*, and finely-divided-titanium-oxide powder was caught with the bag filter made from polytetrafluoroethylene after introducing cooling air into a coil so that material gas might be stagnated for 0.04 second.

[0056]The obtained titanium oxide was put into the hot wind circulation heating furnace, and the dechlorination was carried out to water with the titanium oxide mass ratio 0.06 and the cooking temperature at 450 \*\*. In this way, the water extraction chlorine content was [ the BET specific surface area / 1,200 mass ppm and the total chlorine content of the obtained titanium oxide of  $44\text{m}^2/\text{g}$  and rutile content ] 1,300 mass ppm 12%. It is a water extraction chlorine content to a formula (1). 1,200 mass ppm, total chlorine content The rate of surface chlorine computed by substituting 1,300 mass ppm was higher than 80%, and total chlorine content showed the numerical value smaller than the value computed by substituting specific surface area  $^2$ [ of  $44\text{ m}^2/\text{g}$  for a formula (2). The diameter D90 of 90% accumulation mass particle size distribution in the particle size distribution measured by the laser diffraction type particle-size-distribution measuring method of this powder was 1.2 micrometers. The rate of rutile-izing, a BET specific surface area, a total chlorine content, the rate of surface chlorine, D90 and Fe, aluminum, Si, and the analysis result of S are shown in Table 1.

Comparative example 4: Pure water washed the precipitate obtained by boiling a commercial titanyl sulfate solution (the Kanto Kagaku make, the 1st class of reagent), and hydrous titanium oxide was obtained. In order to remove residual sulfuric acid of this hydrous titanium oxide, pure water was added and it was considered as the slurry, and the aqueous ammonia solution was added, the pH to 5



was adjusted, stirring this, and it stirred for 12 hours. Then, hydrous titanium oxide concentration was condensed to 20 mass % by ultrafiltration membrane. filtering by ultrafiltration membrane, adjusting the pH to 5 and adding [ add an aqueous ammonia solution to a concentrate again, ] pure water after 12-hour stirring -- a titania -- sol was obtained. the obtained titania -- sol was dried at 300 \*\* for 2 hours, and ultrafine particle titanium oxide by a liquid phase process was obtained. The BET specific surface areas of the obtained titanium oxide were 212m<sup>2</sup>/g and 1% of rutile content. Both the water extraction chlorine content and the total chlorine content were 0 mass ppm. When this titanium oxide was cracked with the mortar and particle size distribution was measured by the laser diffraction type particle-size-distribution measuring method, the 90% accumulation mass particle size D90 was 26.1 micrometers. The rate of rutile-izing, a BET specific surface area, a total chlorine content, the rate of surface chlorine, D90 and Fe, aluminum, Si, and the analysis result of S are shown in Table 1.

[0057]

[Table 1]

	実施例 1	実施例 2	実施例 3	比較例 1	比較例 2	比較例 3	比較例 4
ルチル化率 %	1	3	1	11	2	12	1
BET比表面積 m <sup>2</sup> /g	22	65	97	19	74	44	212
全塩素含有量 ppm	1,000	1,100	2,000	300	3,900	1,300	<10
表面塩素率 %	90	91	90	100	72	92	—
D90 μm	1.1	1.9	2.2	0.8	3.6	1.2	26.1
Fe ppm	<10	<10	<10	<10	<10	<10	50
Al ppm	<10	<10	<10	<10	<10	<10	<10
Si ppm	<20	<20	<20	<20	<20	<20	<20
S ppm	<10	<10	<10	<10	<10	<10	670

[0058]

[Effect of the Invention]It compares with the conventional titanium oxide which has an equivalent BET specific surface area by this invention, The anatase type ultrafine particle titanium oxide by a gaseous phase method whose halogen content inside particles was low and which was excellent in especially dispersibility, Titanium oxide of 2.5 micrometers or less and these manufacturing methods are provided for D90 measured by titanium oxide and the laser diffraction type particle-size-distribution measuring method with which the relation between a BET specific surface area (B) and halogen content (C) is satisfied of the conditions of said formula (2) by carrying out dehalogenation of this.

[0059]Since dispersibility [ especially as opposed to / titanium oxide of this invention is suitable for a photocatalyst use, a solar cell use, etc. and / the solvent of a drainage system ] is excellent, It can use conveniently for an underwater photocatalyst use, a crushing process etc. can be managed with needlessness or very minor equipment also as a granular material, and it has industrial very big practical value.

[Translation done.]



**\* NOTICES \***

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**TECHNICAL FIELD**

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[Field of the Invention]This invention relates to suitable low-salt matter ultrafine particle titanium oxide of a low rutile type for a photocatalyst, a solar cell, the additive agent to silicone rubber, a dielectric use, etc., and a manufacturing method for the same. In the gaseous phase method titanium oxide obtained by carrying out high temperature oxidation of the gas containing halogen titanium with an oxidizing gas in more detail, it is related with good low halogen ultrafine particle titanium oxide of a low rutile type and a manufacturing method for the same of dispersibility easily [ a halogen content is low and / removal of the halogen which remained ].

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[Translation done.]

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**PRIOR ART**

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[Description of the Prior Art]Ultrafine particle titanium oxide has been used [ many uses, such as an ultraviolet-rays shielding material, an additive agent of silicone GOMUHE, a dielectric raw material, and cosmetics, ] (titanium oxide is indicated to be a titanium dioxide to Japanese Industrial Standard (JIS)).

Since titanium oxide is widely used as a general name, in this specification, it is called titanium oxide for short.

Titanium oxide is applied also as a photocatalyst, a solar cell, etc.

[0003]Although a rutile type, an anatase type, and three brookite type kinds exist in the crystal form of titanium oxide, in the above-mentioned photocatalyst and the field of a solar cell use, the anatase type and brookite type which excel a rutile type in photoelectricity chemicals activity are used.

[0004]The photocatalyst effect of titanium oxide is used for disassembly of organic matters, such as an antibacterial tile, self-cleaning building materials, and a deodorizing fiber, and the mechanism is explained as follows. Titanium oxide absorbs ultraviolet rays and makes the inside generate an electron and an electron hole. An electron hole reacts to the water of adsorption of titanium oxide, makes a hydroxy radical generate, and disassembles into carbon dioxide or water the organic matter which stuck to the titanium oxide particle surface ("optical clean revolution" Akira Fujishima, Kazuhito Hashimoto, Toshiya Watabe collaboration, CMC Co., Ltd., 143 - 145 pages (1997)). That is, it being easy to generate an electron hole and arriving [ an electron hole / easily ]-at the titanium oxide surface \*\* are mentioned as conditions for strong titanium oxide of a photocatalyst effect. Anatase type titanium oxide, titanium oxide with few lattice defects, and titanium oxide with large specific surface area with small particles are mentioned to "everything about titanium oxide photocatalysts" (Kazuhito Hashimoto and Fujishima Showa edit, CMC Co., Ltd., 29 - 30 pages (1998)) as titanium oxide with a high photocatalyst effect.

[0005]Since the application as a solar cell reported the dye sensitizing type solar cell with which GURETTSUERU and others of Lausanne College of Engineering combined titanium oxide and ruthenium series coloring matter in 1991, research has been advanced (M. (Grazel, Nature, 353 and 737, 1991)). In said dye sensitizing type solar cell, titanium oxide has a role of the support and the n-type semiconductor of coloring matter, and is used as a coloring matter electrode bound to the electrically-conductive-glass electrode. A dye sensitizing type solar cell is the structure which put the electrolyzer by the coloring matter electrode and the counter electrode, and coloring matter generates an electron and an electron hole by absorbing light. The electron by which it was generated reaches an electrically-conductive-glass electrode through a titanium oxide layer, and is taken out outside. On the other hand, the generated electron hole is carried to a counter electrode through an electrolyzer, and is combined with the electron supplied through the electrically-conductive-glass electrode. As a cause which improves the characteristic of a dye sensitizing type solar cell, it is mentioned that combination of titanium oxide and coloring matter is easy. As a crystal form of titanium oxide with an easy combination with coloring matter, anatase is used for JP,10-255863,A and it is indicated to JP,2000-340269,A, for example that brookite is suitable for a dye sensitizing type solar cell.

[0006]Titanium oxide is important when the good thing of dispersibility pulls out the function. For example, since obliterating power will become strong if dispersibility is bad when using titanium oxide as a photocatalyst, the use which can be used will be limited. Since titanium oxide with bad dispersibility in the field of a solar cell cannot penetrate light easily, the titanium oxide which can be contributed to optical absorption is restricted, and it worsens photoelectric conversion efficiency.

Generally, if light scattering (obliterating power) becomes the maximum when particle diameter is about [ of a visible light wavelength ]  $1/2$ , and particle diameter becomes small, it is said that light scattering also becomes weaker ("titanium oxide" Seino \*\*\*\*, Gihodo Shuppan Co., Ltd., Inc., p.129, (1991)). the primary particle diameter of the titanium oxide used in the above-mentioned field -- number -- since it is tens of nm in many cases, if dispersibility is good, the influence on light scattering is small. However, as for titanium oxide with large condensation particle diameter with bad distribution, light scattering will become strong.

[0007]From the above reason, in the above-mentioned field, high dispersibility is required of titanium oxide and the good anatase type of dispersibility or brookite type ultrafine particle titanium oxide is used for it. Generally, the primary particle diameter of an ultrafine particle is usually called to particle of about 0.1 micrometer or less, although it does not clarify.

[0008]If the ingredient which has corrosiveness like chlorine exists, in order to make a substrate corrode or to make it deteriorate when using titanium oxide with a photocatalyst and a solar cell, it is necessary to stop the chlorine content of titanium oxide low. It is better to stop Fe, aluminum, Si, S, etc. low. For example, if there is too much Fe in titanium oxide, it will become a cause of coloring, and it is not suitable for use for the use of which transparency is required. If there are too many ingredients, such as aluminum inside a titanium oxide particle and S, a lattice defect will be produced, and reducing the function as a photocatalyst and a solar cell is also considered.

[0009]The manufacturing method of titanium oxide has a liquid phase process which divides roughly and hydrolyzes titanium tetrachloride and titanyl sulfate, and the gaseous phase method make halogenation titanium react to oxidizing gases, such as oxygen or a steam. Although titanium oxide by a liquid phase process can obtain anatase as a main phase, it cannot but be in sol or a slurry regime. A use is limited when using it in this state. In order to use it as powder, it is necessary to make it dry, and desiccation takes the ultrafine particle which got wet in the solvent for progressing, and condensation becomes intense ("ultrafine particle handbook" Saito [ Susumu ] 6 editorial supervision, a FUJI techno system, 388 pages (1990)). In presenting a photocatalyst etc. with this titanium oxide, in order to improve dispersibility, it is necessary to crack titanium oxide strongly or to grind, and problems originating in processing of grinding etc., such as mixing of a wear thing and unevenness of particle size distribution, may be caused.

[0010]Generally, since a solvent is not used for titanium oxide by a gaseous phase method, it is excellent in dispersibility compared with the liquid phase process.

[0011]There are many examples which obtain the ultrafine particle of titanium oxide by a gaseous phase method, for example, in JP,6-340423,A. In the method of hydrolyzing titanium tetrachloride in a flame and manufacturing titanium oxide, adjust the mole ratio of oxygen, titanium tetrachloride, and hydrogen, it is made to react, and the method of obtaining titanium oxide with high rutile content is indicated. By making titanium tetrachloride hydrolyze into JP,7-316536,A in the elevated-temperature gaseous phase, and cooling a resultant quickly, In the method of manufacturing crystalline-titanium-oxide powder, the way the first [ an average of ] particle diameter obtains crystalline substance transparent titanium oxide (not less than 40 nm and 150 nm or less) is indicated by specifying flame temperature and the titanium concentration in material gas. However, in any case, it is particles, but only titanium oxide with high rutile content is obtained, and it is not suitable for using it as a photocatalyst use and a solar cell use.

[0012]The manufacturing method which adjusts the content ratio of rutile because the way anatase manufactures titanium oxide of a main phase by a gaseous phase method changes the ratio of hydrogen in the gaseous mixture of oxygen and hydrogen into JP,3-252315,A in gaseous phase reaction, for example is indicated.

Titanium oxide whose rutile content is 9% is indicated.

However, the particle diameter of the illustrated titanium oxide is 0.5-0.6 micrometer, and is coarser than the range of the particle diameter generally called ultrafine particle.

[0013]If titanium oxide is manufactured by the gaseous phase method which uses halogenation titanium as a raw material, it will be easy to obtain an ultrafine particle, but since halogen of raw material origin remains in titanium oxide, the dehalogenation by heating or rinsing is needed in many cases. However, sintering of particles advances with heating for low halogenation, and specific surface area falls easily, and also transition of the crystal form to a rutile type [ type / anatase ] may produce ultrafine particle titanium oxide. In order to control the fall of specific surface area, and crystal transition, heating of low temperature or a short time must be performed, but it stops fully

being able to carry out dehalogenation. The low chlorinating method of ultrafine particle titanium oxide is indicated by JP,10-251021,A, for example. This method is the method of making a steam contact, rolling titanium oxide all over a cylindrical shape revolving heating furnace, and making a chlorine content low. The rutile content of the titanium oxide indicated to this was as high as 15%. [0014]On the other hand, although the halogen which remained in the titanium oxide particle surface could be removed in the dehalogenation by rinsing etc., since halogen inside particles was not able to contact water easily, it had the problem that internal halogen remained easily.

[0015]These ultrafine particle titanium oxide of the low rutile type whose halogen content is [ like ] low in the conventional gaseous phase method was not obtained.

[Patent documents 1] JP,10-255863,A[Patent documents 2] JP,2000-340269,A[Patent documents 3] JP,6-340423,A[Patent documents 4] JP,7-316536,A[Patent documents 5] JP,10-251021,A

[Nonpatent literature 1] "Optical clean revolution" Akira Fujishima, Kazuhito Hashimoto, Toshiya Watabe collaboration, CMC Co., Ltd., 143 - 145 pages (1997)

[Nonpatent literature 2] "Everything about titanium oxide photocatalysts" (Kazuhito Hashimoto and Fujishima Showa edit, CMC Co., Ltd., 29 - 30 pages (1998))

[Nonpatent literature 3] M.Graezel,Nature,353,737,(1991)

[Nonpatent literature 4] "Titanium oxide" Seino \*\*\*\*, Gihodo Shuppan Co., Ltd., Inc., p.129 (1991),

[Nonpatent literature 5] ("Ultrafine particle handbook" Saito [ Susumu ] 6 editorial supervision, a FUJI techno system, 388 pages (1990))

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**EFFECT OF THE INVENTION**

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[Effect of the Invention]It compares with the conventional titanium oxide which has an equivalent BET specific surface area by this invention, The anatase type ultrafine particle titanium oxide by a gaseous phase method whose halogen content inside particles was low and which was excellent in especially dispersibility, Titanium oxide of 2.5 micrometers or less and these manufacturing methods are provided for D90 measured by titanium oxide and the laser diffraction type particle-size-distribution measuring method with which the relation between a BET specific surface area (B) and halogen content (C) is satisfied of the conditions of said formula (2) by carrying out dehalogenation of this.

[0059]Since dispersibility [ especially as opposed to / titanium oxide of this invention is suitable for a photocatalyst use, a solar cell use, etc. and / the solvent of a drainage system ] is excellent, It can use conveniently for an underwater photocatalyst use, a crushing process etc. can be managed with needlessness or very minor equipment also as a granular material, and it has industrial very big practical value.

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**TECHNICAL PROBLEM**

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[Problem(s) to be Solved by the Invention]This invention is made that the above-mentioned problem should be solved, and there is a technical problem of this invention in excelling in dispersibility and providing ultrafine particle titanium oxide of a low rutile type with a low halogen content, and a manufacturing method for the same in a gaseous phase method.

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**MEANS**

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[Means for Solving the Problem]As a result of inquiring wholeheartedly in view of an aforementioned problem, this invention persons find out that it excels in dispersibility and ultrafine particle titanium oxide of a low rutile type with a low halogen content can be manufactured in a gaseous phase method, and came to solve an aforementioned problem.

[0018]In a gaseous phase method to which gas and a oxidizing gas (mixed gas containing oxygen, a steam, or these) with which this invention contains halogenation titanium are made to react, . After making this material gas react, controlling cooking temperature and cooking time, are obtained by carrying out dehalogenation. Ultrafine particle titanium oxide of a low rutile type which rutile content is 5% or less of titanium oxide, and has a high BET specific surface area and the specific characteristic, and a manufacturing method for the same are provided.

[0019]That is, this invention includes the following inventions.

- (1) Are titanium oxide obtained by making gas and a oxidizing gas containing halogenation titanium react, and rutile content at 5% or less. And when B ( $\text{m}^2/\text{g}$ ) and a total halogen content of titanium oxide are set to C (mass ppm) for specific surface area of titanium oxide measured with a BET one point method for BET method, Titanium oxide when it is shown by  $C \leq 650e^{0.02B}$  and is considered as aqueous suspension of 1 mass %, wherein halogen more than 80 mass % of the amount of halogen contained in titanium oxide after neglect for 30 minutes at 20 \*\* shifts the aqueous suspension to the liquid phase.
- (2) Titanium oxide given in the above (1) in which halogen more than 90 mass % of the amount of halogen contained in titanium oxide shifts to the liquid phase.
- (3) Titanium oxide the above (1) in which titanium oxide contains each element of Fe, aluminum, Si, and S below 100 mass ppm, respectively, or given in (2).
- (4) Titanium oxide given in above-mentioned (1) - (3) in which titanium oxide has the specific surface area of 10-200- $\text{m}^2/\text{g}$ .
- (5) Titanium oxide given in any 1 paragraph of above-mentioned (1) - (4) whose main phase of titanium oxide is anatase.
- (6) Titanium oxide given in the above (5) whose anatase content of titanium oxide is not less than 90%.
- (7) Titanium oxide given in any 1 paragraph of above-mentioned (1) - (4) whose main phase of titanium oxide is brookite.
- (8) Titanium oxide of the above (7) whose brookite content of titanium oxide is not less than 90%.
- (9) Titanium oxide given in any 1 paragraph of above-mentioned (1) - (8) in which titanium oxide has a diameter of 90% accumulation mass particle size distribution of 2.5 micrometers or less measured with a laser diffraction type grading analysis meter.
- (10) Titanium oxide given in any 1 paragraph of above-mentioned (1) - (9) said whose halogenation titanium is titanium tetrachloride and in which said halogen is chlorine.
- (11) In the gaseous phase method for manufacturing titanium oxide by making gas and a oxidizing gas containing halogenation titanium react, A manufacturing method of titanium oxide in which temperature in this reactor is characterized by not less than 800 \*\* being less than 1,100 \*\* when gas and a oxidizing gas containing halogenation titanium are introduced into a reactor, respectively and are made to react.
- (12) A manufacturing method of titanium oxide given in the above (11) whose with a not less than 800 \*\* [ temperature below 1,100 \*\* ] holding time gas and a oxidizing gas containing halogenation



titanium is 0.1 or less second within a reactor.

(13) A manufacturing method of titanium oxide the above (11) which gas and a oxidizing gas containing halogenation titanium are preheated by not less than 600 \*\* and less than 1,100 \*\*, respectively, and is introduced into a reactor, or given in (12).

(14) a reaction -- halogenation -- titanium -- one -- mol -- receiving -- inactive gas -- 0.1 - 20 -- mol -- a rate -- having mixed -- material gas -- halogenation -- titanium -- one -- mol -- receiving -- one - 30 -- mol -- a oxidizing gas -- carrying out -- having -- the above -- (--- 11 ---) - (--- 13 ---) -- some -- one -- a paragraph -- a statement -- titanium oxide -- a manufacturing method .

(15) A manufacturing method of titanium oxide given in any 1 paragraph of above-mentioned (11) - (14), wherein a oxidizing gas is oxygen gas containing a steam.

(16) A manufacturing method of titanium oxide given in the above (15) in which a oxidizing gas contains 0.1 mol or more of steams to 1 mol of oxygen gas.

(17) A manufacturing method of titanium oxide given in any 1 paragraph of above-mentioned (11) - (16) in which said halogenation titanium is titanium tetrachloride.

(18) The above (11) Manufacturing method of titanium oxide removing halogen for titanium oxide manufactured with a manufacturing method given in any 1 paragraph of - (17) by dry type.

(19) A manufacturing method of titanium oxide given in the above (18) whose method of removing halogen by dry type is the method of performing by heating titanium oxide at 200-500 \*\*.

(20) A manufacturing method of titanium oxide given in the above (18) whose method of removing halogen by dry type is the method of performing while heating gas containing a steam at 200-1000 \*\* and making titanium oxide contact.

(21) A manufacturing method of titanium oxide given in the above (20) which is the air in which gas containing a steam contains a steam in more than 0.1 capacity %.

(22) A manufacturing method of titanium oxide given in the above (20) whose steam is 0.01 or more in a mass ratio to titanium oxide.

(23) The above (11) Manufacturing method of titanium oxide obtaining a slurry which removes halogen for titanium oxide manufactured with a manufacturing method given in any 1 paragraph of - (17) by a wet type, and contains titanium oxide.

(24) A manufacturing method of titanium oxide given in the above (23) which is the method of separating halogen in which a method of removing halogen by a wet type made titanium oxide suspended in water, and shifted to the liquid phase out of a system.

(25) A manufacturing method of titanium oxide the above (23) whose method of removing halogen by a wet type is a method of separating halogen by ultrafiltration membrane, or given in (24).

(26) A manufacturing method of titanium oxide the above (23) whose method of removing halogen by a wet type is a method of separating halogen by a reverse osmotic membrane, or given in (24).

(27) A manufacturing method of titanium oxide the above (23) whose method of removing halogen by a wet type is a way the filter press separates halogen, or given in (24).

(28) The above (11) Granular material by which titanium oxide manufactured with a manufacturing method of a statement being included in any 1 paragraph of - (27).

(29) The above (11) Slurry by which titanium oxide manufactured with a manufacturing method of a statement being included in any 1 paragraph of - (27).

(30) The above (11) Constituent by which titanium oxide manufactured with a manufacturing method of a statement being included in any 1 paragraph of - (27).

(31) The above (11) Photocatalyst material by which titanium oxide manufactured with a manufacturing method of a statement being included in any 1 paragraph of - (27).

(32) The above (11) Charge of wet solar cell material by which titanium oxide manufactured with a manufacturing method of a statement being included in any 1 paragraph of - (27).

(33) The above (11) Dielectric raw material by which titanium oxide manufactured with a manufacturing method of a statement being included in any 1 paragraph of - (27).

(34) The above (11) Silicone rubber additive agent by which titanium oxide manufactured with a manufacturing method of a statement being included in any 1 paragraph of - (27).

Specific surface area which rutile content measured with a BET one point method for BET method 5% or less (35)  $10-200\text{m}^2/\text{g}$ , A diameter of 90% accumulation mass particle size distribution measured with a laser diffraction type grading analysis meter is a titanium oxide particle of 2.5 micrometers or less, And when a halogen content inside B ( $\text{m}^2/\text{g}$ ) and a titanium oxide particle is made into C<sub>i</sub> (mass

ppm) for specific surface area of titanium oxide measured with a BET one point method for BET method, A titanium oxide particle, wherein the amount of halogen contained in an inside of particles is shown by  $0 < C_i \leq 650k e^{0.02B}$  (k is 0.20).

(36) A titanium oxide particle given in the above (35) which contains in an inside of particles halogen of quantity shown by  $10 < C_i \leq 650k e^{0.02B}$  (k is 0.15).

[0020]

[Embodiment of the Invention]As halogenation titanium which is a raw material of titanium oxide of this invention, the titanium chloride which is easy to come to hand industrially, especially titanium tetrachloride are preferred. Therefore, although the case where halogen is chlorine about this invention is hereafter explained as an example of representation, this invention can be applied also when halogen is bromine or iodine. In spite of manufacturing low rutile type ultrafine particle titanium oxide of this invention using titanium tetrachloride by a gaseous phase method, chlorine hardly exists in the inside of particles. Although the chlorine which remains inside particles is temporally diffused from the inside of a particle to the surface, it may corrode and a substrate may be deteriorated, in easy dechlorination of rinsing, desiccation, etc., it is hard to remove. Therefore, it is desirable for chlorine not to exist in the inside of a titanium oxide particle. About the chlorine content inside the particles occupied to the inside of the sum total chlorinity inside a particle surface and particles, the ratio of the chlorine (water extraction chlorine is called) extracted from titanium oxide with pure water and all the chlorine (all the chlorine is called) contained in a titanium oxide particle is made into an index, and it is a lower type (1).

$R = WCL / TCL \times 100 \dots\dots\dots(1)$

(R expresses the rate of surface chlorine (%) among a formula, WCL expresses the content (mass %) of the water extraction chlorine contained in titanium oxide, and TCL expresses the content (mass %) of all the chlorine contained in titanium oxide.) -- it is shown that there is so little chlorine content inside a titanium oxide particle that the value of R expressed is high. About titanium oxide in this invention, it is desirable still more preferred that R is not less than 80%, and it is not less than 90%.

[0021]The ultrafine particle titanium oxide obtained by the gaseous phase method which uses titanium tetrachloride of this invention as a raw material is rutile content.[The peak height corresponding to a rutile type crystal [ in / in rutile content / an X diffraction ] (it carries out abbreviated to Hr.), The ratio computed from the peak height (it carries out abbreviated to Hb.) corresponding to a brookite type crystal, and the peak height (it carries out abbreviated to Ha.) corresponding to an anatase type crystal (=  $100 \times Hr / (Hr + Ha + Hb)$  is said.) ] is 5% or less of ultrafine particle titanium oxide (it may be hereafter called for short ultrafine particle titanium oxide of a low rutile type.), and it is following general formula (2):  $C \leq 650k e^{0.02B}$  also before a dechlorination step not only depending on after a dechlorination step but depending on the case. ....(2)

It comes out and has a total chlorine content expressed. C shows a total chlorine content (mass %) among a formula. C measures the liquid which added fluoric acid solution to titanium oxide, and carried out heating and dissolving to it with microwave, for example with the potentiometric titration by silver nitrate, obtains the mass of chlorine in titanium oxide, and is obtained by \*(ing) with the mass of titanium oxide using this. B expresses a BET specific surface area ( $m^2/g$ ), and the range is  $10-200m^2/g$ . It has the characteristic of being expressed.

[0022]That is, ultrafine particle titanium oxide of a low rutile type of this invention is titanium oxide with few total chlorine contents with which it is satisfied of the conditions of the above-mentioned general formula (2) in drawing 1, and R of the above-mentioned formula (1) is a titanium oxide particle with small chlorine content inside large particles. Ultrafine particle titanium oxide by the gaseous phase method which uses conventional titanium tetrachloride as a raw material, Even if it is a low rutile type titanium dioxide, it is what has the characteristic of the field plotted by the upper part of the curve expressed with  $C = 650k e^{0.02B}$  shown in drawing 1 in the relation between a BET specific surface area and a total chlorine content, It was a titanium oxide particle whose chlorine content inside the above-mentioned particles is also large further again. In particular, the dechlorination of the titanium oxide with larger specific surface area is hard to be carried out, and it has a tendency which a chlorine content increases exponentially.

[0023]As for the low rutile type titanium dioxide of this invention, the relation between a chlorine content and a BET specific surface area satisfies the characteristic of a general formula (2), it is an

ultrafine particle — usually — the range of a BET specific surface area —  $10\text{--}200\text{m}^2/\text{g}$  — they are  $40\text{--}200\text{m}^2/\text{g}$  and a thing which has the range of  $45\text{--}120\text{m}^2/\text{g}$  still more preferably.

[0024]ultrafine particle titanium oxide of a low rutile type of this invention — the content of Fe, aluminum, Si, and S — below 100 mass each ppm — desirable — each 0.1 to 100 mass ppm — more — desirable — each 0.1 to 50 mass ppm — it is each 0.1 to 10 mass ppm still more preferably. In order for such impurity concentration to be less than 0.1 ppm, raw material which manufactures titanium oxide is made into a high grade, and it is necessary in equipment construction material to use a corrosion-resistant high thing more etc. It is economically more advantageous for titanium oxide of this invention not to carry out each impurity less than 0.1 mass ppm in the use usually used.

[0025]The low rutile type titanium dioxide of this invention is characterized by dispersibility being high. In this invention, the laser diffraction type particle-size-distribution measuring method was adopted as an index of dispersibility, and particle size distribution was measured. According to "ultrafine particle handbook" Saito [ Susumu ] 6 editorial supervision, a FUJI techno system, p93, and (1990), there are a sedimentation method, a microscopic method, light scattering measurement, a direct count method, etc. in the measuring method of dispersibility, but. Among these, a sedimentation method and a direct count method are not less than hundreds of nm, and their measurable particle diameter is unsuitable for measuring the dispersibility of an ultrafine particle. Since measured value is changed by the sampling of an object sample, or pretreatment of a sample, a microscopic method cannot be said as a desirable measuring method, either. On the other hand, light scattering measurement can measure particle diameter in several nanometers – several micrometers, and are suitable for measurement of the ultrafine particle. The measurement procedure of particle size distribution is explained below.

[0026]Ultrasonic irradiation (46 kHz, 65W) is carried out to the slurry which added 50 ml of pure water, and 10% sodium hexametaphosphate solution 100mul to the titanium oxide 0.05g for 3 minutes. Particle size distribution is measured applying this slurry to a laser diffraction type size distribution measuring device (Shimadzu Corp. make SALD-2000J). Thus, if the value of the diameter of 90% accumulation mass particle size distribution in the measured particle size distribution (it may be hereafter written as D90) is small, it will be judged that good dispersibility is shown to a hydrophilic solvent. Although it is also possible to make the diameter of accumulation mass particle size distribution into the index of dispersibility 50%, it is hard to detect the bad floc of dispersibility, and is not desirable. As for ultrafine particle titanium oxide of this invention, it is preferred that D90 is 2.5 micrometers or less.

[0027]Finely divided titanium oxide of this invention is contained as a particle component using the raw material, paints, or photocatalyst effect of various constituents, for example, can be used as the raw material of various products, such as cosmetics, an ultraviolet-rays shielding material, a dielectric or silicone rubber, and a solar cell, and an additive agent.

[0028]Next, a manufacturing method is explained. The manufacturing method of common titanium oxide by a gaseous phase method is publicly known, and if titanium tetrachloride is oxidized under about 1,000 \*\* reaction condition using oxidizing gases, such as oxygen or a steam, particulate titanium oxide will be obtained.

[0029]In order to obtain titanium oxide of an ultrafine particle in a gaseous phase method, growth time (growth zone) of particles must be shortened. That is, the grain growth by sintering etc. can be stopped by performing cooling, dilution, etc. promptly after a reaction and shortening elevated-temperature holding time as much as possible. It leads also to shortening of elevated-temperature holding time controlling the heat rearrangement to rutile from anatase, and particles with high anatase content can be obtained.

[0030]In the titanium oxide generally obtained by the gaseous phase method which uses titanium tetrachloride as a raw material, chlorine of 0.1 – 2 mass % usually remains. The chlorine content to which the point which can combine chlorine etc. remains in a titanium oxide particle surface when those (the above-mentioned Seino \*\*\*\* "titanium oxide") with  $13\text{-piece } [/\text{nm}]^2$  and all these joints are chlorinating is theoretically expressed in the anatase-type-titanium-oxide surface by the lower type (3).

$Y=0.077 \times A \dots (3)$

(Y shows among a formula the chlorine content (mass %) which remains in a titanium oxide particle surface, and A shows specific surface area ( $\text{m}^2/\text{g}$ ).)

For example, according to said formula (3), the chlorine content which remains in the titanium oxide particle surface which has the specific surface area of  $100\text{--m}^2/\text{g}$  becomes about 8 mass %.

[0031]In practice, that chlorine and a oxidizing gas replace at a reaction, and when chlorine carries out balanced movement according to the level-of-chlorine difference of a titanium oxide particle surface and the gaseous phase, the chlorine content of titanium oxide may become low a little rather than the value obtained by said formula (3), but. It is considered that shortening of the elevated-temperature holding time in a reaction does not complete oxidation reaction of titanium tetrachloride, and makes the titanium oxide in which a part is chlorinated increased. Since residual chlorine also becomes increasing the chlorinity inside the grain child left behind inside a titanium oxide particle, the heat-treatment which chlorine removal takes will turn an elevated temperature and for a long time, and will produce the fall of specific surface area. Therefore, although a chlorine content is high [ the ultrafine particle conventionally obtained by a gaseous phase method / of what has high anatase content ], or low, it is said that anatase content is low.

[0032]In the gaseous phase method for manufacturing titanium oxide by reacting the gas and the oxidizing gas containing titanium tetrachloride in this invention (high temperature oxidation), The oxidizing gas heated at the gas containing the titanium tetrachloride heated at not less than 600 \*\* less than 1,100 \*\* and not less than 600 \*\* less than 1,100 \*\* is supplied to a coil, respectively, By making the titanium oxide produced by making react stagnate in the time for 0.1 or less second, and a coil on the not less than 800 \*\* high temperature conditions below 1,100 \*\*, In the relation between a BET specific surface area and a chlorine content, low rutile type ultrafine particle titanium oxide with low total chlorine content, especially chlorine content inside particles is obtained, It found out that low rutile type ultrafine particle titanium oxide also with a low chlorine content inside particles whose total chlorine content is still lower was obtained by dechlorinating this. Here, there are a dry method and wet process in a dechlorination. A dry type dechlorination method heats titanium oxide using heating apparatus, such as a cylindrical shape revolving heating furnace, a hot wind circle method heating furnace, a fluidized-drying furnace, and a churning drying furnace, and has a method of removing chlorine, for example. This invention is not necessarily limited to these heating apparatus. A wet dechlorination method makes titanium oxide suspended to pure water, and has a method of separating the chlorine which shifted to the liquid phase out of a system, for example. After separating chlorine out of a system, the obtained titanium oxide may be dried.

[0033]Not less than 800 \*\* less than 1,100 \*\* is desirable still more preferred, and the temperature in the coil which introduces titanium tetrachloride content gas or a oxidizing gas is not less than 900 \*\* less than 1,000 \*\*. By making the degree of coil internal temperature high, simultaneously with mixing, since it completes, uniform karyogenesis is increased, and the reaction can make a reaction (CVD) zone small. If the degree of coil internal temperature is lower than 800 \*\*, although titanium oxide with high anatase content will be easy to be obtained, a reaction is insufficient and chlorine remains inside a titanium oxide particle. If the degree of coil internal temperature will be not less than 1,100 \*\*, rutile transition and particle growth will advance and a low rutile type and an ultrafine particle will not be obtained.

[0034]Since this reaction is an exoergic reaction on the other hand when material gas is introduced into a coil and a reaction advances, the reaction zones where reaction temperature exceeds 1,100 \*\* exist. Although there is some device heat dissipation, unless it quenches, a titanium oxide particle will grow rapidly and a crystal form will transfer it to rutile. Then, in this invention, not less than 800 \*\* elevated-temperature holding time below 1,100 \*\* is especially made into the range for 0.01 to 0.05 second preferably for 0.005 to 0.1 second 0.1 or less second. If elevated-temperature holding time exceeds 0.1 second, since transition to rutile and sintering of particles will advance, it is not desirable. Since elevated-temperature holding time becomes short [ the oxidation reaction time of titanium tetrachloride ] in less than 0.005 second, it is necessary to carry out under the conditions which are easy to perform oxidation, such as using the amount of oxygen superfluous enough compared with titanium tetrachloride. If oxidation is insufficient, it leads to the increase in residual chlorinity inside particles.

[0035]As a means of quenching, the method of introducing gas, such as a lot of cooling air and nitrogen, into a reaction mixture, for example or the method of spraying water is adopted.

[0036]Rutile transition and grain growth can be controlled by being able to obtain an ultrafine particle with a low chlorine content inside particles by controlling the temperature in a coil at said not less than 800 \*\* less than 1,100 \*\*, and controlling elevated-temperature holding time at 0.1 or less

second.

[0037]In order for the temperature in a coil to be said not less than 800 \*\* less than 1,100 \*\*, it is preferred to adjust the cooking temperature of material gas to not less than 600 \*\* 1,100 \*\* or less. Although the heated material gas reacts and generates heat within a coil, the temperature in a coil cannot be not less than 800 \*\* easily for material gas temperature to be less than 600 \*\*. Although there is device heat dissipation that material gas temperature is not less than 1,100 \*\*, the temperature in a coil becomes easy to exceed 1,100 \*\*.

[0038]It is desirable still more preferred that it is 0.1–20 mol of inactive gas to 1 mol of gaseous titanium tetrachlorides, and the material gas presentation containing titanium tetrachloride is 4–20 mol. When there is less inactive gas than said range, the titanium oxide particle density in reaction zones increases, and since it condenses and becomes easy to sinter, ultrafine particle titanium oxide is hard to be obtained. When there is more inactive gas than said range, reactivity falls and the recovery rate as titanium oxide falls.

[0039]As for the amount of oxygen gas made to react to the material gas containing titanium tetrachloride, it is preferred that it is 1–30 mol to 1 mol of titanium tetrachloride. It is 5–30 mol still more preferably. If the amount of oxygen gas is increased, an ultrafine particle will become the number of karyogenesis increases and is easy to be obtained, but even if it exceeds 30 mol, most effects of making the number of karyogenesis increasing cannot be found. Even if the amount of oxygen gas exceeds 30 mol, it is uninfluential in the characteristic of titanium oxide, but a maximum is set up from an economical viewpoint. On the other hand, if the amounts of oxygen gas run short to titanium tetrachloride, it will be titanium oxide with many oxygen deficiencies, and will color. The steam other than oxygen may be contained in the oxidizing gas. Although each gas which mixed inactive gas (nitrogen, argon, etc.) can use it for oxygen, oxygen containing a steam, air, and these oxidizing gases, for example, since reaction temperature tends to control a oxidizing gas, its oxygen containing a steam is preferred.

[0040]As for the dechlorination by heating of titanium oxide, it is preferred to carry out with the not less than 200 \*\* cooking temperature at 500 \*\* or less, contacting a steam to titanium oxide powder so that the mass ratio (the mass/titanium oxide of = steam are the same as that of mass and the following) of water and titanium oxide may become 0.01 or more. Preferably, the mass ratio of water and titanium oxide is 0.04 or more, and cooking temperature is not less than 250 \*\* 450 \*\* or less. If cooking temperature exceeds 500 \*\*, sintering of a titanium oxide particle will progress and grain growth will arise. If cooking temperature is less than 200 \*\*, the efficiency of a dechlorination will fall extremely. A dechlorination runs and goes, when chlorine on the surface of titanium oxide carries out a substitution reaction to the water near the particle, or the adjoining surface–water–of–aggregate acid radical of particles. When chlorine of a titanium oxide particle surface is replaced by water, it is dechlorinated, without carrying out grain growth, but when replaced by the surface–water–of–aggregate acid radical of the adjoining particles, grain growth will be carried out simultaneously with a dechlorination. Since the probability which carries out a substitution reaction to the particle surface hydroxyl group in which it adjoins as titanium oxide especially with large specific surface area becomes high, it is easy to carry out grain growth. That is, in order to attain dechlorination, controlling grain growth, the mass ratio of water and titanium oxide is also important, and if the mass ratio of water and titanium oxide is 0.01 or more, the effect which controls grain growth will be accepted.

[0041]As for the steam contacted to titanium oxide, it is preferred to use it, mixing with the gas which has a role which moves efficiently the chlorine separated from titanium oxide out of a system. As such gas, air is mentioned, for example. When using air, as for a steam, it is desirable still more preferred that more than 0.1 capacity % is contained in air, and more than 5 capacity % is more than 10 capacity % especially preferably. As for the air having contained the steam, it is preferred to heat at not less than 200 \*\* 1,000 \*\* or less.

[0042]Since chlorine hardly exists in the inside of particles, low rutile type ultrafine particle titanium oxide by this invention can also form low-salt base by a wet type. Titanium oxide is made suspended to pure water, and the way ultrafiltration membrane, a reverse osmotic membrane, the filter press, etc. separate the chlorine which shifted to the liquid phase out of a system is mentioned to the wet dechlorination method, for example. Thus, low rutile type ultrafine particle titanium oxide with a total halogen content and the halogen content inside particles low in the relation of the BET specific surface area of this invention and halogen content which are manufactured, By carrying out

dehalogenation of the halogen of a particle surface more nearly thoroughly preferably, low rutile type ultrafine particle titanium oxide whose total halogen content is very low can be obtained in a relation with a BET specific surface area. Therefore, low rutile type ultrafine particle titanium oxide of this invention, The specific surface area which rutile content measured with the BET one point method for BET method 5% or less like the above  $10\text{--}200\text{m}^2/\text{g}$ , The diameter of 90% accumulation mass particle size distribution measured with a laser diffraction type grading analysis meter is a titanium oxide particle of 2.5 micrometers or less, And when the halogen content inside B ( $\text{m}^2/\text{g}$ ) and a titanium oxide particle is made into  $C_i$  (mass ppm) for the specific surface area of the titanium oxide measured with the BET one point method for BET method, The amount of halogen contained in the inside of particles  $0 \leq C_i \leq 650k e^{0.02B}$  (k is 0.20), It is preferably characterized by  $0 < C_i \leq 650k e^{0.02B}$  (k is 0.20) and the thing more preferably shown by  $10 < C_i \leq 650k e^{0.02B}$  (k is 0.15).

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**EXAMPLE**

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[Example]Although an example and a comparative example explain concretely hereafter, this invention is not limited to these at all.

[0044]Example 1:1.8Nm<sup>3</sup>/hr (N means a normal condition.) It is below the same. The titanium tetrachloride dilution gas which diluted gaseous titanium tetrachloride with the nitrogen gas of 8-Nm<sup>3</sup>/hr is preheated at 900 \*\*, The oxidizing gas which mixed oxygen of 8-Nm<sup>3</sup>/hr and a 32-Nm<sup>3</sup>/hr steam was preheated at 800 \*\*, and these material gas was introduced into the reactor made from silica glass. As it had been 0.1 second about the not less than 800 \*\* elevated-temperature holding time below 1,100 \*\*, finely-divided-titanium-oxide powder was caught with the bag filter made from polytetrafluoroethylene after introducing cooling air into a coil.

[0045]The dechlorination of the obtained titanium oxide was carried out to the cylindrical shape revolving heating furnace with the mass ratio 0.02 of through, water, and titanium oxide, and the cooking temperature at 450 \*\*. Then, the water extraction chlorine content was [ the BET specific surface area / 900 mass ppm and the total chlorine content of the obtained titanium oxide of 22m<sup>2</sup>/g and a rutile content ratio (it is also called rutile content.) ] 1,000 mass ppm 1%. However, a BET specific surface area is measured with the Shimadzu surface area measuring instrument (models are flow SOBU II and 2300), The peak height corresponding to a rutile type crystal [ in / in a rutile content ratio / an X diffraction ] (it carries out abbreviated to Hr.), It is the ratio (=100xHr/(Hr+Ha+Hb)) computed from the peak height (it carries out abbreviated to Hb.) corresponding to a brookite type crystal, and the peak height (it carries out abbreviated to Ha.) corresponding to an anatase type crystal. It is a water extraction chlorine content to a formula (1). 900 mass ppm, total chlorine content The rate of surface chlorine computed by substituting 1,000 mass ppm was higher than 80%, and the total chlorine content showed the numerical value smaller than the value computed by substituting specific surface area <sup>2</sup>[ of 22 m ]/g for a formula (2).

[0046]It was 1.1 micrometers as a result of measuring the diameter D90 of accumulation mass particle size distribution 90% by a laser diffraction type particle-size-distribution measuring method about the particle size distribution of the titanium oxide powder obtained here. The rate of rutile-izing, a BET specific surface area, a total chlorine content, the rate of surface chlorine, D90 and Fe, aluminum, Si, and the analysis result of S are shown in Table 1.

[0047]The titanium tetrachloride dilution gas which diluted gaseous titanium tetrachloride of example 2:5.9Nm<sup>3</sup>/hr with the nitrogen gas of 30-Nm<sup>3</sup>/hr is preheated at 1,000 \*\*, The oxidizing gas which mixed oxygen of 4-Nm<sup>3</sup>/hr and the steam of 16-Nm<sup>3</sup>/hr was preheated at 1,000 \*\*, and these material gas was introduced into the reactor made from silica glass. As it had been 0.03 second about the not less than 800 \*\* elevated-temperature holding time below 1,100 \*\*, finely-divided-titanium-oxide powder was caught with the bag filter made from polytetrafluoroethylene after introducing cooling air into a coil.

[0048]The obtained titanium oxide was put into the hot wind circulation heating furnace, and the dechlorination was carried out to water with the titanium oxide mass ratio 0.04 and the cooking temperature at 450 \*\*. In this way, the water extraction chlorine content was [ the BET specific surface area / 900 mass ppm and the total chlorine content of the obtained titanium oxide of 65m<sup>2</sup>/g and rutile content ] 1,100 mass ppm 3%. It is a water extraction chlorine content to a formula (1). 900 mass ppm, total chlorine content The rate of surface chlorine computed by substituting 1,100 mass ppm was higher than 80%, and the total chlorine content showed the numerical value smaller than the



value computed by substituting specific surface area  $^2$ [ of 65 m ]/g for a formula (2). The diameter D90 of 90% accumulation mass particle size distribution in the particle size distribution measured by the laser diffraction type particle-size-distribution measuring method of this powder was 1.9 micrometers. The rate of rutile-izing, a BET specific surface area, a total chlorine content, the rate of surface chlorine, D90 and Fe, aluminum, Si, and the analysis result of S are shown in Table 1.

[0049]The titanium tetrachloride dilution gas which diluted gaseous titanium tetrachloride of example 3:4.7Nm<sup>3</sup>/hr with the nitrogen gas of 36-Nm<sup>3</sup>/hr is preheated at 1,000 \*\*, The oxidizing gas which mixed the air of 36-Nm<sup>3</sup>/hr and the steam of 25-Nm<sup>3</sup>/hr was preheated at 1,000 \*\*, and these material gas was introduced into the reactor made from silica glass. As it had been 0.02 second about the not less than 800 \*\* elevated-temperature holding time below 1,100 \*\*, finely-divided-titanium-oxide powder was caught with the bag filter made from polytetrafluoroethylene after introducing cooling air into a coil.

[0050]The obtained titanium oxide was put into the hot wind circulation heating furnace, and the dechlorination was carried out to water with the titanium oxide mass ratio 0.06 and the cooking temperature at 350 \*\*. In this way, water extraction chlorine content was [ the BET specific surface area / 1,800 mass ppm and the total chlorine content of the obtained titanium oxide of 97m<sup>2</sup>/g and rutile content ] 2,000 mass ppm 1%. It is a water extraction chlorine content to a formula (1). 1,800 mass ppm, total chlorine content The rate of surface chlorine computed by substituting 2,000 mass ppm was higher than 80%, and total chlorine content showed the numerical value smaller than the value computed by substituting specific surface area  $^2$ [ of 97 m ]/g for a formula (2). The diameter D90 of 90% accumulation mass particle size distribution in the particle size distribution measured by the laser diffraction type particle-size-distribution measuring method of this powder was 2.2 micrometers. The rate of rutile-izing, a BET specific surface area, a total chlorine content, the rate of surface chlorine, D90 and Fe, aluminum, Si, and the analysis result of S are shown in Table 1.

[0051]The titanium tetrachloride dilution gas which diluted gaseous titanium tetrachloride of comparative example 1:11.8Nm<sup>3</sup>/hr with the nitrogen gas of 8-Nm<sup>3</sup>/hr is preheated at 900 \*\*, The oxidizing gas which mixed oxygen of 8-Nm<sup>3</sup>/hr and a 32-Nm<sup>3</sup>/hr steam was preheated at 800 \*\*, and these material gas was introduced into the reactor made from silica glass. As it had been 0.2 second about the not less than 800 \*\* elevated-temperature holding time below 1,100 \*\*, finely-divided-titanium-oxide powder powder was caught with the bag filter made from polytetrafluoroethylene after introducing cooling air into a coil.

[0052]The dechlorination of the obtained titanium oxide was carried out to through and water in the cylindrical shape revolving heating furnace with the titanium oxide mass ratio 0.02 and the cooking temperature at 450 \*\*. In this way, the water extraction chlorine content was [ the BET specific surface area / 300 mass ppm and the total chlorine content of the obtained titanium oxide of 19m<sup>2</sup>/g and a rutile content ratio ] 300 mass ppm 11%. It is water extraction chlorine content to a formula (1). 300 mass ppm, total chlorine content The rate of surface chlorine computed by substituting 300 mass ppm was higher than 80%, and total chlorine content showed the numerical value smaller than the value computed by substituting specific surface area  $^2$ [ of 19 m ]/g for a formula (2). The diameter D90 of 90% accumulation mass particle size distribution in the particle size distribution measured by the laser diffraction type particle-size-distribution measuring method of this powder was 0.8 micrometer. The rate of rutile-izing, a BET specific surface area, a total chlorine content, the rate of surface chlorine, D90 and Fe, aluminum, Si, and the analysis result of S are shown in Table 1.

[0053]The titanium tetrachloride dilution gas which diluted gaseous titanium tetrachloride of comparative example 2:4.7Nm<sup>3</sup>/hr with the nitrogen gas of 36-Nm<sup>3</sup>/hr is preheated at 800 \*\*, The oxidizing gas which mixed the air of 36-Nm<sup>3</sup>/hr and the steam of 25-Nm<sup>3</sup>/hr was preheated at 800 \*\*, and these material gas was introduced into the reactor made from silica glass. This coil temperature was controlled at 750 \*\*, and finely-divided-titanium-oxide powder was caught with the bag filter made from polytetrafluoroethylene after introducing cooling air into a coil so that material gas might be stagnated for 0.08 second.

[0054]The obtained titanium oxide was put into the hot wind circulation heating furnace, and the dechlorination was carried out to water with the titanium oxide mass ratio 0.04 and the cooking temperature at 350 \*\*. In this way, water extraction chlorine content was [ the BET specific surface

area / 2,800 mass ppm and the total chlorine content of the obtained titanium oxide of  $74\text{m}^2/\text{g}$  and rutile content ] 3,900 mass ppm 2%. It is a water extraction chlorine content to a formula (1). 2,800 mass ppm, total chlorine content The rate of surface chlorine computed by substituting 3,900 mass ppm was lower than 80%, and total chlorine content showed the bigger numerical value than the value computed by substituting specific surface area  $^2$ [ of  $74\text{ m}^2/\text{g}$  for a formula (2). The diameter D90 of 90% accumulation mass particle size distribution in the particle size distribution measured by the laser diffraction type particle-size-distribution measuring method of this powder was 3.6 micrometers. The rate of rutile-izing, a BET specific surface area, a total chlorine content, the rate of surface chlorine, D90 and Fe, aluminum, Si, and the analysis result of S are shown in Table 1.

[0055]The titanium tetrachloride dilution gas which diluted gaseous titanium tetrachloride of comparative example 3: $5.9\text{Nm}^3/\text{hr}$  with the nitrogen gas of  $30\text{-Nm}^3/\text{hr}$  is preheated at  $1,100^\circ\text{C}$ , The oxidizing gas which mixed oxygen of  $4\text{-Nm}^3/\text{hr}$  and the steam of  $16\text{-Nm}^3/\text{hr}$  was preheated at  $1,100^\circ\text{C}$ , and these material gas was introduced into the reactor made from silica glass. This coil temperature was controlled at  $1,200^\circ\text{C}$ , and finely-divided-titanium-oxide powder was caught with the bag filter made from polytetrafluoroethylene after introducing cooling air into a coil so that material gas might be stagnated for 0.04 second.

[0056]The obtained titanium oxide was put into the hot wind circulation heating furnace, and the dechlorination was carried out to water with the titanium oxide mass ratio 0.06 and the cooking temperature at  $450^\circ\text{C}$ . In this way, the water extraction chlorine content was [ the BET specific surface area / 1,200 mass ppm and the total chlorine content of the obtained titanium oxide of  $44\text{m}^2/\text{g}$  and rutile content ] 1,300 mass ppm 12%. It is a water extraction chlorine content to a formula (1). 1,200 mass ppm, total chlorine content The rate of surface chlorine computed by substituting 1,300 mass ppm was higher than 80%, and total chlorine content showed the numerical value smaller than the value computed by substituting specific surface area  $^2$ [ of  $44\text{ m}^2/\text{g}$  for a formula (2). The diameter D90 of 90% accumulation mass particle size distribution in the particle size distribution measured by the laser diffraction type particle-size-distribution measuring method of this powder was 1.2 micrometers. The rate of rutile-izing, a BET specific surface area, a total chlorine content, the rate of surface chlorine, D90 and Fe, aluminum, Si, and the analysis result of S are shown in Table 1.

Comparative example 4: Pure water washed the precipitate obtained by boiling a commercial titanyl sulfate solution (the Kanto Kagaku make, the 1st class of reagent), and hydrous titanium oxide was obtained. In order to remove residual sulfuric acid of this hydrous titanium oxide, pure water was added and it was considered as the slurry, and the aqueous ammonia solution was added, the pH to 5 was adjusted, stirring this, and it stirred for 12 hours. Then, hydrous titanium oxide concentration was condensed to 20 mass % by ultrafiltration membrane. filtering by ultrafiltration membrane, adjusting the pH to 5 and adding [ add an aqueous ammonia solution to a concentrate again, ] pure water after 12-hour stirring -- a titania -- sol was obtained. the obtained titania -- sol was dried at  $300^\circ\text{C}$  for 2 hours, and ultrafine particle titanium oxide by a liquid phase process was obtained. The BET specific surface areas of the obtained titanium oxide were  $212\text{m}^2/\text{g}$  and 1% of rutile content. Both the water extraction chlorine content and the total chlorine content were 0 mass ppm. When this titanium oxide was cracked with the mortar and particle size distribution was measured by the laser diffraction type particle-size-distribution measuring method, the 90% accumulation mass particle size D90 was 26.1 micrometers. The rate of rutile-izing, a BET specific surface area, a total chlorine content, the rate of surface chlorine, D90 and Fe, aluminum, Si, and the analysis result of S are shown in Table 1.

[0057]

[Table 1]

	実施例 1	実施例 2	実施例 3	比較例 1	比較例 2	比較例 3	比較例 4
ルチル化率 %	1	3	1	11	2	12	1
BET比表面積 $\text{m}^2/\text{g}$	22	65	97	19	74	44	212
全塩素含有量 質量 ppm	1,000	1,100	2,000	300	3,900	1,300	<10
表面塩素率 %	90	91	90	100	72	92	—
D90 $\mu\text{m}$	1.1	1.9	2.2	0.8	3.6	1.2	26.1
Fe 質量 ppm	<10	<10	<10	<10	<10	<10	50
Al 質量 ppm	<10	<10	<10	<10	<10	<10	<10
Si 質量 ppm	<20	<20	<20	<20	<20	<20	<20
S 質量 ppm	<10	<10	<10	<10	<10	<10	670

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**DESCRIPTION OF DRAWINGS**

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[Brief Description of the Drawings]

[Drawing 1]The relation between the halogen content of finely divided titanium oxide and a BET specific surface area is shown.

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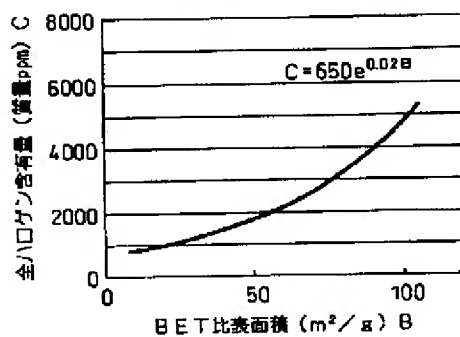
DRAWINGS

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[Drawing 1]

図1

比表面積とハロゲン濃度



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[Translation done.]

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最終頁に続く

(54) 【発明の名称】 低ハロゲン低ルチル型超微粒子酸化チタン及びその製造方法

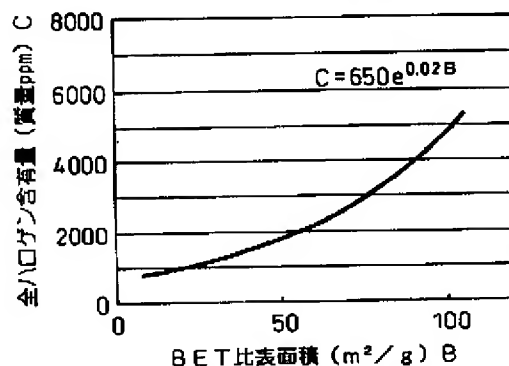
(57) 【要約】

【課題】 気相法において、分散性に優れ、かつハロゲン含有量の低い低ルチル型の超微粒子酸化チタン及びその製造方法を提供する。

【解決手段】 ハロゲン化チタンを含有するガス及び酸化性ガスを反応させる気相法において、該原料ガスを加熱温度、加熱時間を制御しながら反応させた後、脱ハロゲンすることにより、ルチル含有率が5%以下の酸化チタンであって、かつ、高いBET比表面積及び特定の特性を有する低ルチル型の超微粒子酸化チタンを得る。

図1

比表面積とハロゲン濃度



## 【特許請求の範囲】

【請求項1】 ハロゲン化チタンを含むガスと酸化性ガスとを反応させることにより得られる酸化チタンであって、ルチル含有率が5%以下で、かつ、BET一点法で測定した酸化チタンの比表面積を $B$  ( $\text{m}^2/\text{g}$ )、酸化チタンの全ハロゲン含有量を $C$  (質量ppm)としたとき、

$$C \leq 650 e^{0.02B}$$

で示され、且つ、1質量%の水懸濁液とした時に、その水懸濁液を20℃で30分間放置後、酸化チタンに含まれていたハロゲン量の80質量%以上のハロゲンが液相に移行することを特徴とする酸化チタン。

【請求項2】 酸化チタンに含まれていたハロゲン量の90質量%以上のハロゲンが液相に移行する請求項1に記載の酸化チタン。

【請求項3】 酸化チタンが、Fe、Al、Si及びSの各元素をそれぞれ100質量ppm以下含む請求項1または2に記載の酸化チタン。

【請求項4】 酸化チタンが、 $10 \sim 200 \text{ m}^2/\text{g}$ の比表面積を持つ請求項1乃至3に記載の酸化チタン。

【請求項5】 酸化チタンの主相が、アナターゼである請求項1乃至4に記載の酸化チタン。

【請求項6】 酸化チタンのアナターゼ含有率が、90%以上である請求項5に記載の酸化チタン。

【請求項7】 酸化チタンの主相が、ブルッカイトである請求項1乃至4に記載の酸化チタン。

【請求項8】 酸化チタンのブルッカイト含有率が90%以上である請求項7の酸化チタン。

【請求項9】 酸化チタンが、レーザー回折式粒度分析計によって測定される $2.5 \mu\text{m}$ 以下の90%累積質量粒度分布径を持つ、請求項1乃至8のいずれか1項に記載の酸化チタン。

【請求項10】 前記ハロゲン化チタンが四塩化チタンであり、前記ハロゲンが塩素である請求項1乃至9のいずれか1項に記載の酸化チタン。

【請求項11】 ハロゲン化チタンを含むガスと酸化性ガスとを反応させることにより酸化チタンを製造する気相法において、ハロゲン化チタンを含むガス及び酸化性ガスをそれぞれ反応器に導入し反応させたとき、該反応器内の温度が800℃以上1,100℃未満であることを特徴とする酸化チタンの製造方法。

【請求項12】 ハロゲン化チタンを含むガス及び酸化性ガスが、反応器内で800℃以上1,100℃未満の温度の滞留時間が0.1秒以下である請求項11に記載の酸化チタンの製造方法。

【請求項13】 ハロゲン化チタンを含むガス及び酸化性ガスが、それぞれ、600℃以上、1,100℃未満に予熱されて反応器に導入される請求項11または12に記載の酸化チタンの製造方法。

【請求項14】 反応が、ハロゲン化チタン1モルに対

し不活性ガス0.1～20モルの割合で混合した原料ガスと、ハロゲン化チタン1モルに対し1～30モルの酸化性ガスとで行われる請求項11乃至13のいずれか1項に記載の酸化チタンの製造方法。

【請求項15】 酸化性ガスが、水蒸気を含む酸素ガスであることを特徴とする請求項11乃至14のいずれか1項に記載の酸化チタンの製造方法。

【請求項16】 酸化性ガスが、酸素ガス1モルに対し、水蒸気0.1モル以上を含む請求項15に記載の酸化チタンの製造方法。

【請求項17】 前記ハロゲン化チタンが四塩化チタンである請求項11乃至16のいずれか1項に記載の酸化チタンの製造方法。

【請求項18】 請求項11乃至17のいずれか1項に記載の製造方法で製造された酸化チタンを乾式でハロゲンを除去することを特徴とする酸化チタンの製造方法。

【請求項19】 乾式でハロゲンを除去する方法が、酸化チタンを200～500℃に加熱することにより行う方法である請求項18に記載の酸化チタンの製造方法。

【請求項20】 乾式でハロゲンを除去する方法が、水蒸気を含有するガスを200～1000℃に加熱し、酸化チタンと接触させながら行なう方法である請求項18に記載の酸化チタンの製造方法。

【請求項21】 水蒸気を含有するガスが、水蒸気を0.1容量%以上含む空気である請求項20に記載の酸化チタンの製造方法。

【請求項22】 水蒸気が、酸化チタンに対し質量比で0.01以上である請求項20に記載の酸化チタンの製造方法。

【請求項23】 請求項11乃至17のいずれか1項に記載の製造方法で製造された酸化チタンを湿式でハロゲンを除去し、酸化チタンを含むスラリーを得ることを特徴とする酸化チタンの製造方法。

【請求項24】 湿式でハロゲンを除去する方法が、酸化チタンを水に懸濁させ、液相に移行したハロゲンを系外に分離する方法である請求項23に記載の酸化チタンの製造方法。

【請求項25】 湿式でハロゲンを除去する方法が、ハロゲンの分離を限外ろ過膜で行う方法である請求項23または24に記載の酸化チタンの製造方法。

【請求項26】 湿式でハロゲンを除去する方法が、ハロゲンの分離を逆浸透膜で行う方法である請求項23または24に記載の酸化チタンの製造方法。

【請求項27】 湿式でハロゲンを除去する方法が、ハロゲンの分離をフィルタープレスで行う方法である請求項23または24に記載の酸化チタンの製造方法。

【請求項28】 請求項11乃至27のいずれか1項に記載の製造方法で製造された酸化チタンを含むことを特徴とする粉体。

【請求項29】 請求項11乃至27のいずれか1項に



記載の製造方法で製造された酸化チタンを含むことを特徴とするスラリー。

【請求項30】 請求項11乃至27のいずれか1項に記載の製造方法で製造された酸化チタンを含むことを特徴とする組成物。

【請求項31】 請求項11乃至27のいずれか1項に記載の製造方法で製造された酸化チタンを含むことを特徴とする光触媒材料。

【請求項32】 請求項11乃至27のいずれか1項に記載の製造方法で製造された酸化チタンを含むことを特徴とする湿式太陽電池用材料。

【請求項33】 請求項11乃至27のいずれか1項に記載の製造方法で製造された酸化チタンを含むことを特徴とする誘電体原料。

【請求項34】 請求項11乃至27のいずれか1項に記載の製造方法で製造された酸化チタンを含むことを特徴とするシリコンゴム添加剤。

【請求項35】 ルチル含有率が5%以下、BET一点法で測定した比表面積が $10 \sim 200 \text{ m}^2/\text{g}$ 、レーザー回折式粒度分析計によって測定される90%累積質量粒度分布径が $2.5 \mu\text{m}$ 以下の酸化チタン粒子であり、かつ、BET一点法で測定した酸化チタンの比表面積を $B (\text{m}^2/\text{g})$ 、酸化チタン粒子内部のハロゲン含有量を $C_i$  (質量ppm)としたとき、粒子内部に含まれるハロゲン量が $0 \leq C_i \leq 650 \text{ ke}^{0.025}$  ( $k$ は0.20)で示されることを特徴とする酸化チタン粒子。

【請求項36】  $10 < C_i \leq 650 \text{ ke}^{0.025}$  ( $k$ は0.15)で示される量のハロゲンを粒子内部に含む請求項35に記載の酸化チタン粒子。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、光触媒や太陽電池、シリコンゴムへの添加剤、誘電体用途等に好適な低ルチル型の低塩素超微粒子酸化チタン及びその製造方法に関する。さらに詳しくは、ハロゲンチタンを含むガスを酸化性ガスで高温酸化することにより得られる気相法酸化チタンにおいて、ハロゲン含有量が低く、残存したハロゲンの除去も容易で、かつ、分散性の良い低ルチル型の低ハロゲン超微粒子酸化チタン及びその製造方法に関する。

【0002】

【従来の技術】超微粒子酸化チタンは、紫外線遮蔽材やシリコンゴムへの添加剤、誘電体原料、化粧料等、多岐の用途に亘って使用されてきた(酸化チタンは日本工業規格(JIS)には二酸化チタンと記載されており、一般名として酸化チタンが広く使用されているので本明細書中では酸化チタンと略称する)。また、酸化チタンは光触媒や、太陽電池等としても応用される。

【0003】酸化チタンの結晶型にはルチル型、アナターゼ型、ブルッカイト型の3種類が存在するが、このう

ち、前述の光触媒、太陽電池用途の分野ではルチル型よりも光電気化学活性に優れるアナターゼ型やブルッカイト型が用いられる。

【0004】酸化チタンの光触媒作用は抗菌タイル、セルフ・クリーニング建材、消臭繊維など、有機物の分解に利用されており、その機構は次のように説明されている。酸化チタンは紫外線を吸収し、その内部に電子と正孔を発生させる。正孔は酸化チタンの吸着水と反応してヒドロキシラジカルを生成させ、酸化チタン粒子表面に吸着した有機物を炭酸ガスや水に分解する(「光クリーン革命」藤嶋昭、橋本和仁、渡部俊也共著、(株)シーエムシー、143-145頁(1997))。すなわち、光触媒作用の強い酸化チタンの条件として、正孔を発生させやすいこと、酸化チタン表面に正孔が到達しやすいこと、が挙げられる。「酸化チタン光触媒のすべて」(橋本和仁、藤嶋昭 編集、(株)シーエムシー、29-30頁(1998))には、光触媒作用が高い酸化チタンとして、アナターゼ型酸化チタン、格子欠陥の少ない酸化チタン、粒子が小さく比表面積の大きい酸化チタンが挙げられている。

【0005】太陽電池としての応用は、1991年にローザンヌ工科大学のグレッツェルらが酸化チタンとルテニウム系色素を組み合わせた色素増感型太陽電池を報告して以来、研究が進められている(M. Graetzel, Nature, 353, 737, (1991))。前記色素増感型太陽電池において、酸化チタンは色素の担持体及びn型半導体としての役割を有し、導電性ガラス電極に結着された色素電極として用いられる。色素増感型太陽電池は電解層を色素電極と対極で挟み込んだ構造であり、色素は光を吸収することで電子と正孔を発生する。発生した電子は酸化チタン層を通じて導電性ガラス電極に到達し、外部へと取り出される。一方、発生した正孔は、電解層を通じて対極へと運ばれ、導電性ガラス電極を通じて供給された電子と結合する。色素増感型太陽電池の特性を高める一因として、酸化チタンと色素の結合が容易であることが挙げられる。色素との結合が容易な酸化チタンの結晶型としては、例えば、特開平10-255863号公報にはアナターゼが使用されており、また、特開2000-340269号公報にはブルッカイトが色素増感型太陽電池に好適であることが記載されている。

【0006】酸化チタンは分散性の良いものがその機能を引き出す上で重要である。例えば酸化チタンを光触媒として使用する際、分散性が悪いと隠蔽力が強くなるため、使用できる用途が限定されてしまう。太陽電池の分野においても分散性の悪い酸化チタンは光を透過しにくいため、光吸収に寄与できる酸化チタンが限られ、光電変換効率を悪化させる。一般に、光散乱(隠蔽力)は粒径が可視光波長の $1/2$ 程度であるとき最大になり、粒径が小さくなると光散乱も弱まるといわれている(「酸

化チタン」清野学著、技報堂（株）、p. 129, (1991)）。前述の分野で利用される酸化チタンの一次粒子径は数～数十nmであることが多いため分散性が良好であれば光散乱への影響は小さい。しかし、分散が悪く凝集粒径の大きい酸化チタンは光散乱が強まることになる。

【0007】以上の理由から上記分野では、酸化チタンには高分散性が要求され、分散性の良いアナターゼ型あるいはブルッカイト型の超微粒子酸化チタンが使用される。一般に、超微粒子の1次粒子径は、明確にされていないが、通常約0.1μm以下の微粒子に対して呼称される。

【0008】酸化チタンを光触媒、太陽電池で使用する場合、塩素のように腐食性を有する成分が存在すると基材を腐食させたり、変質させたりするため、酸化チタンの塩素含有量は低く抑える必要がある。また、Fe、Al、Si、S等も低く抑えた方がよい。例えば、酸化チタン中のFeが多すぎると着色の原因になり、透明性を要求される用途での使用に適さない。酸化チタン粒子内部のAl、S等の成分が多すぎると格子欠陥を生じてしまい、光触媒、太陽電池としての機能を低下させることも考えられる。

【0009】酸化チタンの製造方法は、大別して四塩化チタンや硫酸チタニルを加水分解する液相法と、ハロゲン化チタンを酸素あるいは水蒸気等の酸化性ガスと反応させる気相法とがある。液相法による酸化チタンはアナターゼを主相として得ることはできるが、ゾルあるいはスラリー状態にならざるを得ない。この状態で使用する場合、用途は限定される。粉末として使用するためには乾燥させる必要があり、溶媒に濡れた超微粒子は乾燥が進むに連れて凝集が激しくなる（「超微粒子ハンドブック」斎藤進六監修、フジ・テクノシステム、388頁、（1990））。この酸化チタンを光触媒等に供する場合には分散性を高めるため酸化チタンを強く解砕したり粉砕する必要がある、粉砕等の処理に由来する摩擦物の混入や粒度分布の不均一さ等の問題を引き起こすことがある。

【0010】一般的に、気相法による酸化チタンは、溶媒を使用しないため液相法に比べて分散性に優れている。

【0011】気相法で酸化チタンの超微粒子を得る例は数多くあり、例えば、特開平6-340423号公報では、四塩化チタンを火炎中にて加水分解し酸化チタンを製造する方法において、酸素、四塩化チタン、水素のモル比を調整して反応させ、ルチル含有率の高い酸化チタンを得る方法が開示されている。特開平7-316536号公報には四塩化チタンを高温気相中で加水分解させ、反応生成物を急速に冷却することにより、結晶質酸化チタン粉末を製造する方法において、炎温度と原料ガス中のチタン濃度を特定することにより平均一次粒子径

が40nm以上、150nm以下の結晶質透明酸化チタンを得る方法が開示されている。しかし、何れの場合も微粒子ではあるがルチル含有率の高い酸化チタンしか得られていなく、光触媒用途、太陽電池用途として使用するには適さない。

【0012】気相法でアナターゼが主相の酸化チタンを製造する方法は、例えば、特開平3-252315号公報には気相反応において酸素と水素の混合気体中の水素の比率を変えることでルチルの含有比率を調整する製造方法が開示されており、ルチル含有率が9%の酸化チタンが記載されている。しかし、例示された酸化チタンの粒径は0.5～0.6μmであり、一般的に超微粒子といわれる粒径の範囲よりも粗い。

【0013】ハロゲン化チタンを原料とする気相法で酸化チタンを製造すると超微粒子は得やすいが、原料由来のハロゲンが酸化チタンに残存するため、加熱あるいは水洗等による脱ハロゲンが必要となることが多い。しかし、超微粒子酸化チタンは低ハロゲン化のための加熱によって粒子同士の焼結が進行し比表面積が低下しやすくなる上、アナターゼ型からルチル型への結晶型の転移が生じてしまうことがある。比表面積の低下、結晶転移を抑制するためには低温あるいは短時間の加熱を行わざるを得ないが、十分に脱ハロゲンできなくなる。超微粒子酸化チタンの低塩素化法は、例えば、特開平10-251021号公報に開示されている。この方法は、酸化チタンを円筒形回転式加熱炉中で転動させながら水蒸気と接触させ、塩素含有量を低くする方法である。また、これに記載されている酸化チタンのルチル含有率は15%と高いものであった。

【0014】一方、水洗等による脱ハロゲンでは酸化チタン粒子表面に残存したハロゲンを除去することはできるが、粒子内部のハロゲンは水と接触しにくい、内部ハロゲンが残存しやすいという問題があった。

【0015】これらのように従来の気相法において、ハロゲン含有量の低い低ルチル型の超微粒子酸化チタンは得られていなかった。

【特許文献1】特開平10-255863号公報

【特許文献2】特開2000-340269号公報

【特許文献3】特開平6-340423号公報

【特許文献4】特開平7-316536号公報

【特許文献5】特開平10-251021号公報

【非特許文献1】「光クリーン革命」藤嶋昭、橋本和仁、渡部俊也共著、（株）シーエムシー、143-145頁（1997）

【非特許文献2】「酸化チタン光触媒のすべて」（橋本和仁、藤嶋昭 編集、（株）シーエムシー、29-30頁（1998））

【非特許文献3】M. Graezel, Nature, 353, 737, (1991)

【非特許文献4】「酸化チタン」清野学著、技報堂

(株), p. 129, (1991)

【非特許文献5】(「超微粒子ハンドブック」斎藤進六監修、フジ・テクノシステム、388頁、(1990))

#### 【0016】

【発明が解決しようとする課題】本発明は上記問題点を解決すべくなされたものであり、本発明の課題は、気相法において、分散性に優れ、かつハロゲン含有量の低い低ルチル型の超微粒子酸化チタン及びその製造方法を提供することにある。

#### 【0017】

【課題を解決するための手段】本発明者らは、上記課題に鑑み鋭意研究した結果、気相法において分散性に優れ、かつ、ハロゲン含有量の低い低ルチル型の超微粒子酸化チタンを製造し得ることを見出し、上記課題を解決するに至った。

【0018】本発明は、ハロゲン化チタンを含有するガス及び酸化性ガス(酸素または水蒸気もしくはこれらを含有する混合ガス)を反応させる気相法において、該原料ガスを加熱温度、加熱時間を制御しながら反応させた後、脱ハロゲンすることにより得られる、ルチル含有率が5%以下の酸化チタンであって、かつ、高いBET比表面積及び特定の特性を有する低ルチル型の超微粒子酸化チタン及びその製造方法を提供するものである。

【0019】すなわち本発明は、以下の発明を含む。

(1) ハロゲン化チタンを含むガスと酸化性ガスとを反応させることにより得られる酸化チタンであって、ルチル含有率が5%以下で、かつ、BET一点法で測定した酸化チタンの比表面積を $B$  ( $\text{m}^2/\text{g}$ )、酸化チタンの全ハロゲン含有量を $C$  (質量ppm)としたとき、 $C \leq 650e^{0.02B}$

で示され、且つ、1質量%の水懸濁液とした時に、その水懸濁液を20℃で30分間放置後、酸化チタンに含まれていたハロゲン量の80質量%以上のハロゲンが液相に移行することを特徴とする酸化チタン。

(2) 酸化チタンに含まれていたハロゲン量の90質量%以上のハロゲンが液相に移行する上記(1)に記載の酸化チタン。

(3) 酸化チタンが、Fe、Al、Si及びSの各元素をそれぞれ100質量ppm以下含む上記(1)または(2)に記載の酸化チタン。

(4) 酸化チタンが、 $10 \sim 200 \text{ m}^2/\text{g}$ の比表面積を持つ上記(1)～(3)に記載の酸化チタン。

(5) 酸化チタンの主相が、アナターゼである上記

(1)～(4)のいずれか1項に記載の酸化チタン。

(6) 酸化チタンのアナターゼ含有率が、90%以上である上記(5)に記載の酸化チタン。

(7) 酸化チタンの主相が、ブルッカイトである上記

(1)～(4)のいずれか1項に記載の酸化チタン。

(8) 酸化チタンのブルッカイト含有率が90%以上である上記(7)の酸化チタン。

(9) 酸化チタンが、レーザー回折式粒度分析計によって測定される $2.5 \mu\text{m}$ 以下の90%累積質量粒度分布径を持つ、上記(1)～(8)のいずれか1項に記載の酸化チタン。

(10) 前記ハロゲン化チタンが四塩化チタンであり、前記ハロゲンが塩素である上記(1)～(9)のいずれか1項に記載の酸化チタン。

(11) ハロゲン化チタンを含むガスと酸化性ガスとを反応させることにより酸化チタンを製造する気相法において、ハロゲン化チタンを含むガス及び酸化性ガスをそれぞれ反応器に導入し反応させたとき、該反応器内の温度が800℃以上1,100℃未満であることを特徴とする酸化チタンの製造方法。

(12) ハロゲン化チタンを含むガス及び酸化性ガスが、反応器内で800℃以上1,100℃未満の温度の滞留時間が0.1秒以下である上記(11)に記載の酸化チタンの製造方法。

(13) ハロゲン化チタンを含むガス及び酸化性ガスが、それぞれ、600℃以上、1,100℃未満に予熱されて反応器に導入される上記(11)または(12)に記載の酸化チタンの製造方法。

(14) 反応が、ハロゲン化チタン1モルに対し不活性ガス0.1～20モルの割合で混合した原料ガスと、ハロゲン化チタン1モルに対し1～30モルの酸化性ガスとで行われる上記(11)～(13)のいずれか1項に記載の酸化チタンの製造方法。

(15) 酸化性ガスが、水蒸気を含む酸素ガスであることを特徴とする上記(11)～(14)のいずれか1項に記載の酸化チタンの製造方法。

(16) 酸化性ガスが、酸素ガス1モルに対し、水蒸気0.1モル以上を含む上記(15)に記載の酸化チタンの製造方法。

(17) 前記ハロゲン化チタンが四塩化チタンである上記(11)～(16)のいずれか1項に記載の酸化チタンの製造方法。

(18) 上記(11)～(17)のいずれか1項に記載の製造方法で製造された酸化チタンを乾式でハロゲンを除去することを特徴とする酸化チタンの製造方法。

(19) 乾式でハロゲンを除去する方法が、酸化チタンを200～500℃に加熱することにより行う方法である上記(18)に記載の酸化チタンの製造方法。

(20) 乾式でハロゲンを除去する方法が、水蒸気を含むガスを200～1000℃に加熱し、酸化チタンと接触させながら行なう方法である上記(18)に記載の酸化チタンの製造方法。

(21) 水蒸気を含むガスが、水蒸気を0.1容量%以上含む空気である上記(20)に記載の酸化チタンの製造方法。

(22) 水蒸気が、酸化チタンに対し質量比で0.01以上である上記(20)に記載の酸化チタンの製造方

法。

(23) 上記(11)～(17)のいずれか1項に記載の製造方法で製造された酸化チタンを湿式でハロゲンを除去し、酸化チタンを含むスラリーを得ることを特徴とする酸化チタンの製造方法。

(24) 湿式でハロゲンを除去する方法が、酸化チタンを水に懸濁させ、液相に移行したハロゲンを系外に分離する方法である上記(23)に記載の酸化チタンの製造方法。

(25) 湿式でハロゲンを除去する方法が、ハロゲンの分離を限外ろ過膜で行う方法である上記(23)または(24)に記載の酸化チタンの製造方法。

(26) 湿式でハロゲンを除去する方法が、ハロゲンの分離を逆浸透膜で行う方法である上記(23)または(24)に記載の酸化チタンの製造方法。

(27) 湿式でハロゲンを除去する方法が、ハロゲンの分離をフィルタープレスで行う方法である上記(23)または(24)に記載の酸化チタンの製造方法。

(28) 上記(11)～(27)のいずれか1項に記載の製造方法で製造された酸化チタンを含むことを特徴とする粉体。

(29) 上記(11)～(27)のいずれか1項に記載の製造方法で製造された酸化チタンを含むことを特徴とするスラリー。

(30) 上記(11)～(27)のいずれか1項に記載の製造方法で製造された酸化チタンを含むことを特徴とする組成物。

(31) 上記(11)～(27)のいずれか1項に記載の製造方法で製造された酸化チタンを含むことを特徴とする光触媒材料。

(32) 上記(11)～(27)のいずれか1項に記載の製造方法で製造された酸化チタンを含むことを特徴とする湿式太陽電池用材料。

(33) 上記(11)～(27)のいずれか1項に記載の製造方法で製造された酸化チタンを含むことを特徴と\*

$$R = WCL / TCL \times 100 \dots\dots\dots (1)$$

(式中、Rは表面塩素率(%)を表し、WCLは酸化チタンに含まれる水抽出塩素の含有量(質量%)を表し、TCLは酸化チタンに含まれる全塩素の含有量(質量%)を表す。)で表されるRの値が高いほど酸化チタン粒子内部の塩素含有率が少ないことを示す。本発明における酸化チタンについて、Rは80%以上であることが好ましく、更に好ましくは90%以上である。

【0021】本発明の四塩化チタンを原料とする気相法によって得られる超微粒子酸化チタンは、ルチル含有率※

$$C \leq 650 \times e^{0.02B} \dots\dots\dots (2)$$

で表される全塩素含有量を有する。式中、Cは全塩素含有量(質量%)を示す。Cは、例えば、酸化チタンにフッ酸水溶液を添加しマイクロウェーブで加熱溶解させた液を、硝酸銀による電位差滴定法で測定し、酸化チタン

\* する誘電体原料。

(34) 上記(11)～(27)のいずれか1項に記載の製造方法で製造された酸化チタンを含むことを特徴とするシリコンゴム添加剤。

(35) ルチル含有率が5%以下、BET一点法で測定した比表面積が $10 \sim 200 \text{ m}^2/\text{g}$ 、レーザー回折式粒度分析計によって測定される90%累積質量粒度分布径が $2.5 \mu\text{m}$ 以下の酸化チタン粒子であり、かつ、BET一点法で測定した酸化チタンの比表面積を $B (\text{m}^2/\text{g})$ 、酸化チタン粒子内部のハロゲン含有量を $C$ 、(質量ppm)としたとき、粒子内部に含まれるハロゲン量が $0 \leq C_1 \leq 650 \text{ ke}^{0.02B}$  (kは0.20)で示されることを特徴とする酸化チタン粒子。

(36)  $10 < C_1 \leq 650 \text{ ke}^{0.02B}$  (kは0.15)で示される量のハロゲンを粒子内部に含む上記(35)に記載の酸化チタン粒子。

【0020】

【発明の実施の形態】本発明の酸化チタンの原料であるハロゲン化チタンとしては、工業的に入手し易い塩化チタン、特に四塩化チタンが好ましい。従って、以下、本発明をハロゲンが塩素の場合を代表例として説明するが、本発明はハロゲンが臭素またはヨウ素である場合にも適用できる。本発明の低ルチル型超微粒子酸化チタンは、気相法で四塩化チタンを用いて製造したものであるにもかかわらず、粒子内部に塩素が殆ど存在しない。粒子内部に残存する塩素は経時的に粒子内部から表面まで拡散し基材を腐食、変質させることがあるが、水洗や乾燥等の簡単な脱塩素処理では除去しにくい。そのため、酸化チタン粒子内部に塩素が存在しないことが望ましい。粒子表面と粒子内部の合計塩素量のうちに占める粒子内部の塩素含有率については、酸化チタンから純水で抽出される塩素(水抽出塩素と称する)と、酸化チタン粒子に含まれる全塩素(全塩素と称する)の比率を指標とし、下式(1)

※ [ルチル含有率は、X線回折におけるルチル型結晶に対応するピーク高さ(Hrと略する。)、ブルックライト型結晶に対応するピーク高さ(Hbと略する。)及びアナターゼ型結晶に対応するピーク高さ(Haと略する。)]から算出した比率(=  $100 \times Hr / (Hr + Ha + Hb)$ )をいう。)が5%以下の超微粒子酸化チタン(以下、低ルチル型の超微粒子酸化チタンと略称することがある。)であり、かつ、脱塩素工程の後のみならず、場合によっては脱塩素工程の前でも、下記一般式(2):

中の塩素の質量を得、これを用いた酸化チタンの質量で除することにより得られる。BはBET比表面積( $\text{m}^2/\text{g}$ )を表し、その範囲は $10 \sim 200 \text{ m}^2/\text{g}$ である。)で表される特性を有することを特徴とする。

【0022】すなわち、本発明の低ルチル型の超微粒子酸化チタンは、図1において上記一般式(2)の条件を満足する全塩素含有量の少ない酸化チタンであり、かつ上記式(1)のRが大きい粒子内部の塩素含有率の小さい酸化チタン粒子である。従来の四塩化チタンを原料とする気相法による超微粒子酸化チタンは、低ルチル型酸化チタンであっても、BET比表面積と全塩素含有量との関係において図1に示した $C=650 \times e^{0.023}$ で表される曲線の上部にプロットされる領域の特性を有しているものであり、さらにまた上記の粒子内部の塩素含有率も大きい酸化チタン粒子であった。特に、比表面積の大きい酸化チタンほど、脱塩素されにくく、塩素含有量が指数関数的に増加する傾向がある。

【0023】本発明の低ルチル型酸化チタンは、塩素含有量とBET比表面積との関係が一般式(2)の特性を満足し、超微粒子であって、通常、BET比表面積の範囲は $10 \sim 200 \text{ m}^2/\text{g}$ 、好ましくは $40 \sim 200 \text{ m}^2/\text{g}$ 、更に好ましくは $45 \sim 120 \text{ m}^2/\text{g}$ の範囲を有するものである。

【0024】また、本発明の低ルチル型の超微粒子酸化チタンは、Fe、Al、Si、Sの含有量が各100質量ppm以下、好ましくは各0.1~100質量ppm、より好ましくは各0.1~50質量ppm、更に好ましくは各0.1~10質量ppmである。これらの不純物濃度を0.1ppm未満にするには、酸化チタンを製造する原材料を高純度とし、また設備材質をより耐食性の高いものを使用すること等が必要となる。本発明の酸化チタンが通常用いられる用途では、各不純物を0.1質量ppm未満としない方が経済的に有利である。

【0025】本発明の低ルチル型酸化チタンは分散性が高いことを特徴とする。本発明においては、分散性の指標としてレーザー回折式粒度分布測定法を採用し粒度分布を測定した。分散性の測定法には、「超微粒子ハンドブック」齋藤進六監修、フジ・テクノシステム、p93、(1990)によると、沈降法、顕微鏡法、光散乱法、直接計数法等があるが、このうち沈降法、直接計数法は測定可能な粒径が数百nm以上であり、超微粒子の分散性を測定するには不適である。また、顕微鏡法も対象試料のサンプリングや試料の前処理によって測定値が変動することもあり、好ましい測定法とはいえない。これに対し、光散乱法は数nm~数 $\mu\text{m}$ の範囲で粒径を測定することができ、超微粒子の測定に適している。粒度分布の測定手順について以下に説明する。

【0026】酸化チタン0.05gに純水50ml及び10%ヘキサメタリン酸ソーダ水溶液100 $\mu\text{l}$ を加えたスラリーに、3分間超音波照射(46KHz、65W)する。このスラリーをレーザー回折式粒度分布測定装置((株)島津製作所製SALD-2000J)にかけて、粒度分布を測定する。このようにして測定された粒度分布における90%累積質量粒度分布径(以下、D

90と略記することがある)の値が小さければ、親水性溶媒に対して良好な分散性を示していると判断される。50%累積質量粒度分布径を分散性の指標とすることも可能であるが、分散性の悪い凝集粒子を検知しにくく好ましくない。本発明の超微粒子酸化チタンは、D90が2.5 $\mu\text{m}$ 以下であることが好ましい。

【0027】本発明の超微粒子状酸化チタンは、各種組成物の原料、顔料または光触媒効果を利用した粒子成分として含まれ、例えば、化粧料、紫外線遮蔽材、誘電体またはシリコーンゴム、太陽電池等、様々な製品の原料、添加剤として利用できる。

【0028】次に製造方法について説明する。気相法による一般的な酸化チタンの製造方法は公知であり、四塩化チタンを酸素または水蒸気等の酸化性ガスを用いて、約1,000℃の反応条件下で酸化させると微粒子酸化チタンが得られる。

【0029】気相法において超微粒子の酸化チタンを得るためには、粒子の成長時間(成長ゾーン)を短くしなければならない。すなわち、反応後速やかに冷却、希釈等を行い、高温滞留時間を極力短くすることにより、焼結等による粒成長を抑えることができる。高温滞留時間の短縮はアナターゼからルチルへの熱転位を抑制することにも繋がり、アナターゼ含有率の高い粒子を得ることができる。

【0030】一般に、四塩化チタンを原料とする気相法で得られる酸化チタンには、通常、0.1~2質量%の塩素が残存している。アナターゼ型酸化チタン表面には、塩素等が結合可能な点が $13 \text{ 個}/\text{nm}^2$ あり(前述の清野学著「酸化チタン」)、この全ての結合点が塩素化している場合、酸化チタン粒子表面に残存する塩素含有量は理論上、下式(3)で表される。

$$Y=0.077 \times A \cdots (3)$$

(式中、Yは酸化チタン粒子表面に残存する塩素含有量(質量%)を示し、Aは比表面積( $\text{m}^2/\text{g}$ )を示す。)

例えば、 $100 \text{ m}^2/\text{g}$ の比表面積を有する酸化チタン粒子表面に残存する塩素含有量は、前記式(3)によれば、約8質量%となる。

【0031】実際は、反応で塩素と酸化性ガスが置換すること、また酸化チタン粒子表面と気相の塩素濃度差によって塩素が平衡移動することにより、酸化チタンの塩素含有量は前記式(3)で得られる値よりも若干低くなる可能性があるが、反応での高温滞留時間の短縮は、四塩化チタンの酸化反応を完結させず、一部が塩素化されたままの酸化チタンを増加させることになると考えられる。また、残存塩素が酸化チタン粒子内部に取り残されると粒子内部の塩素量を増やすことにもなるため、塩素除去に要する加熱処理が高温、長時間化し、比表面積の低下を生じることとなる。従って、従来、気相法によって得られる超微粒子は、アナターゼ含有率の高いものの



塩素含有量が高い、あるいは、塩素含有量は低いがアナターゼ含有率が低いというものであった。

【0032】本発明では、四塩化チタンを含むガスと酸化性ガスとを反応（高温酸化）することにより酸化チタンを製造する気相法において、600℃以上1,100℃未満に加熱した四塩化チタンを含有するガス及び600℃以上1,100℃未満に加熱した酸化性ガスをそれぞれ反応管に供給し、反応させて得られた酸化チタンを800℃以上1,100℃未満の高温条件で0.1秒以下の時間、反応管内に滞留させることにより、BET比表面積と塩素含有量との関係において全塩素含有量、特に粒子内部の塩素含有量が低い低ルチル型超微粒子酸化チタンが得られ、これを脱塩素処理することによりさらに全塩素含有量が低くかつ粒子内部の塩素含有量も低い低ルチル型超微粒子酸化チタンが得られることを見出した。ここで、脱塩素には乾式法と湿式法がある。乾式脱塩素法は、例えば、円筒形回転式加熱炉、熱風循環式加熱炉、流動乾燥炉、攪拌乾燥炉等の加熱装置を用いて酸化チタンを加熱し、塩素を除去する方法がある。尚、本発明は、必ずしもこれら加熱装置に限定されるものではない。また、湿式脱塩素法は、例えば、酸化チタンを純水に懸濁させ、液相に移行した塩素を系外に分離する方法がある。塩素を系外に分離した後、得られた酸化チタンを乾燥しても良い。

【0033】四塩化チタン含有ガスあるいは酸化性ガスを導入する反応管内の温度は800℃以上1,100℃未満が好ましく、更に好ましくは900℃以上1,000℃未満である。反応管内温度を高くすることによって、混合と同時に反応は完結するので均一核発生が増進され、かつ、反応（CVD）ゾーンを小さくすることができる。反応管内温度が800℃より低いと、アナターゼ含有率の高い酸化チタンが得られやすいものの、反応が不十分で酸化チタン粒子内部に塩素が残存する。反応管内温度が1,100℃以上になるとルチル転移や粒子成長が進行し、低ルチル型、超微粒子が得られない。

【0034】一方、原料ガスが反応管に導入され反応が進行すると、本反応が発熱反応である為、反応温度が1,100℃を越える反応ゾーンが存在する。装置放熱は多少あるものの、急冷を施さないかぎり酸化チタン粒子はどんどん成長し、かつ、結晶型がルチルに転移してしまう。そこで、本発明においては800℃以上1,100℃未満の高温滞留時間を0.1秒以下、好ましくは0.005～0.1秒、特に好ましくは0.01～0.05秒の範囲にする。高温滞留時間が0.1秒を越えると、ルチルへの転移や粒子の焼結が進行するので好ましくない。高温滞留時間が0.005秒未満では、四塩化チタンの酸化反応時間も短くなるため、四塩化チタンに比べ十分に過剰な酸素量を用いるなど酸化を行い易い条件下で行う必要がある。酸化が不十分では粒子内部の残存塩素量増加につながる。

【0035】急冷の手段としては、例えば、反応混合物に多量の冷却空気や窒素等のガスを導入する方法、あるいは水を噴霧する方法等が採用される。

【0036】反応管内の温度を前記800℃以上1,100℃未満に制御することで粒子内部の塩素含有量が低い超微粒子を得ることができ、また、高温滞留時間を0.1秒以下に制御することでルチル転移及び粒成長を抑制することができる。

【0037】反応管内の温度を前記800℃以上1,100℃未満にするためには、原料ガスの加熱温度を600℃以上1,100℃以下に調整することが好ましい。加熱された原料ガスは反応管内で反応し発熱するが、原料ガス温度が600℃未満であると、反応管内の温度は800℃以上になりにくい。また、原料ガス温度が1,100℃以上であると装置放熱はあるものの、反応管内の温度は1,100℃を越えやすくなる。

【0038】四塩化チタンを含む原料ガス組成は、四塩化チタンガス1モルに対し、不活性ガス0.1～20モルであることが好ましく、さらに好ましくは4～20モルである。不活性ガスが前記範囲より少ない場合、反応ゾーンにおける酸化チタン粒子密度が高まり、凝集、焼結しやすくなるため、超微粒子酸化チタンが得られにくい。不活性ガスが前記範囲よりも多い場合、反応性が低下し、酸化チタンとしての回収率が低下する。

【0039】四塩化チタンを含む原料ガスと反応させる酸素ガス量は、四塩化チタン1モルに対し1～30モルであることが好ましい。さらに好ましくは5～30モルである。酸素ガス量を増やすと、核発生数が増加し超微粒子は得られやすくなるが、30モルを越えても核発生数を増加させる効果はほとんど無い。酸素ガス量が30モルを越えても酸化チタンの特性に影響は無いが、経済的な観点から上限が設定される。一方、四塩化チタンに対し酸素ガス量が不足すると、酸素欠陥の多い酸化チタンとなり着色してしまう。尚、酸化性ガスには、酸素の他に水蒸気が含まれていても良い。酸化性ガスは、例えば、酸素、水蒸気を含む酸素、空気、これらの酸化性ガスに不活性ガス（窒素、アルゴンなど）を混合したガスがいずれも使用できるが、反応温度の制御しやすいことから水蒸気を含む酸素が好ましい。

【0040】酸化チタンの加熱による脱塩素は、水と酸化チタンとの質量比（＝水蒸気の質量／酸化チタンの質量、以下同様）が0.01以上になるように酸化チタン粉末に水蒸気を接触させながら加熱温度200℃以上500℃以下で行うことが好ましい。更に好ましくは水と酸化チタンの質量比は0.04以上、加熱温度は250℃以上450℃以下である。加熱温度が500℃を越えると酸化チタン粒子の焼結が進み、粒成長が生じる。加熱温度が200℃を下回ると脱塩素の効率が極端に低下する。脱塩素は、酸化チタン表面の塩素が粒子近傍の水あるいは隣接する粒子の表面水酸基と置換反応すること

により進行して行く。酸化チタン粒子表面の塩素が、水と置換された場合には粒成長せずに脱塩素化されるが、隣接する粒子の表面水酸基と置換された場合は脱塩素と同時に粒成長することとなる。特に比表面積の大きい酸化チタンほど隣接する粒子表面水酸基と置換反応する確率が高くなるため、粒成長しやすい。すなわち、粒成長を抑制しつつ脱塩素化を図るためには水と酸化チタンの質量比も重要であり、水と酸化チタンの質量比が0.01以上であれば粒成長を抑制する効果が認められる。

【0041】酸化チタンと接触させる水蒸気は、酸化チタンから分離した塩素を効率良く系外に移動させる役割を有するガスと混合して使用することが好ましい。このようなガスとして、例えば、空気が挙げられる。空気を用いる場合、水蒸気は、空気に0.1容量%以上含まれることが好ましく、更に好ましくは5容量%以上、特に好ましくは10容量%以上である。水蒸気を含んだ空気は200℃以上1,000℃以下に加熱しておくことが好ましい。

【0042】本発明による低ルチル型超微粒子酸化チタンは粒子内部に塩素が殆ど存在しないため、湿式で低塩素化することも可能である。湿式脱塩素方法には、例えば、酸化チタンを純水に懸濁させ、液相に移行した塩素を限外ろ過膜、逆浸透膜、フィルタープレス等によって系外に分離する方法が挙げられる。このようにして製造される本発明のBET比表面積とハロゲン含有量との関係において全ハロゲン含有量および粒子内部のハロゲン含有量の低い低ルチル型超微粒子酸化チタンは、好ましくは粒子表面のハロゲンをより完全に脱ハロゲンすることで、BET比表面積との関係において全ハロゲン含有量が極めて低い低ルチル型超微粒子酸化チタンを得ることができる。従って、本発明の低ルチル型超微粒子酸化チタンは、上記の如く、ルチル含有率が5%以下、BET一点法で測定した比表面積が10~200m<sup>2</sup>/g、レーザー回折式粒度分析計によって測定される90%累積質量粒度分布径が2.5μm以下の酸化チタン粒子であり、かつ、BET一点法で測定した酸化チタンの比表面積をB(m<sup>2</sup>/g)、酸化チタン粒子内部のハロゲン含有量をC<sub>i</sub>(質量ppm)としたとき、粒子内部に含まれるハロゲン量が0≤C<sub>i</sub>≤650ke<sup>0.028</sup> (kは0.20)、好ましくは0<C<sub>i</sub>≤650ke<sup>0.028</sup> (kは0.20)、より好ましくは10<C<sub>i</sub>≤650ke<sup>0.028</sup> (kは0.15)で示されることを特徴とする。

#### 【0043】

【実施例】以下、実施例及び比較例にて具体的に説明するが、本発明はこれらに何ら限定されるものではない。

【0044】実施例1:11.8Nm<sup>3</sup>/hr(Nは標準状態を意味する。以下同じ。)のガス状四塩化チタンを8Nm<sup>3</sup>/hrの窒素ガスで希釈した四塩化チタン希釈ガスを900℃に予熱し、8Nm<sup>3</sup>/hrの酸素と32Nm<sup>3</sup>/hr水蒸気を混合した酸化性ガスを800℃

に予熱し、これらの原料ガスを石英ガラス製反応器に導入した。800℃以上1,100℃未満の高温滞留時間を0.1秒となるように冷却空気を反応管に導入後、ポリテトラフルオロエチレン製バグフィルターにて超微粒子状酸化チタン粉末を捕集した。

【0045】得られた酸化チタンを円筒形回転式加熱炉に通し、水と酸化チタンの質量比0.02、加熱温度450℃で脱塩素した。その後、得られた酸化チタンは、BET比表面積が22m<sup>2</sup>/g、ルチル含有比率(ルチル含有率ともいう。)が1%、水抽出塩素含有量が900質量ppm、全塩素含有量が1,000質量ppmであった。但し、BET比表面積は、島津製作所製比表面積測定装置(機種はフローソープII,2300)で測定し、ルチル含有比率はX線回折におけるルチル型結晶に対応するピーク高さ(H<sub>r</sub>と略する。)、ブルッカイト型結晶に対応するピーク高さ(H<sub>b</sub>と略する。)とアナターゼ型結晶に対応するピーク高さ(H<sub>a</sub>と略する。)から算出した比率(=100×H<sub>r</sub>/(H<sub>r</sub>+H<sub>a</sub>+H<sub>b</sub>))である。式(1)に水抽出塩素含有量900質量ppm、全塩素含有量1,000質量ppmを代入して算出される表面塩素率は80%よりも高く、全塩素含有量は、式(2)に比表面積22m<sup>2</sup>/gを代入して算出される値よりも小さな数値を示した。

【0046】また、ここで得られた酸化チタン粉末の粒度分布について、レーザー回折式粒度分布測定法で90%累積質量粒度分布径D<sub>90</sub>を測定した結果、1.1μmであった。ルチル化率、BET比表面積、全塩素含有量、表面塩素率、D<sub>90</sub>、及び、Fe、Al、Si、Sの分析結果を表1に示す。

【0047】実施例2:5.9Nm<sup>3</sup>/hrのガス状四塩化チタンを30Nm<sup>3</sup>/hrの窒素ガスで希釈した四塩化チタン希釈ガスを1,000℃に予熱し、4Nm<sup>3</sup>/hrの酸素と16Nm<sup>3</sup>/hrの水蒸気を混合した酸化性ガスを1,000℃に予熱し、これらの原料ガスを石英ガラス製反応器に導入した。800℃以上1,100℃未満の高温滞留時間を0.03秒となるように冷却空気を反応管に導入後、ポリテトラフルオロエチレン製バグフィルターにて超微粒子状酸化チタン粉末を捕集した。

【0048】得られた酸化チタンを熱風循環加熱炉に入れ、水と酸化チタン質量比0.04、加熱温度450℃で脱塩素した。こうして得られた酸化チタンは、BET比表面積が65m<sup>2</sup>/g、ルチル含有率が3%、水抽出塩素含有量が900質量ppm、全塩素含有量が1,100質量ppmであった。式(1)に水抽出塩素含有量900質量ppm、全塩素含有量1,100質量ppmを代入して算出される表面塩素率は80%よりも高く、全塩素含有量は、式(2)に比表面積65m<sup>2</sup>/gを代入して算出される値よりも小さな数値を示した。この粉末のレーザー回折式粒度分布測定法にて測定した粒

度分布における90%累積質量粒度分布径D90は1.9 $\mu$ mであった。ルチル化率、BET比表面積、全塩素含有量、表面塩素率、D90、及び、Fe、Al、Si、Sの分析結果を表1に示す。

【0049】実施例3：4.7Nm<sup>3</sup>/hrのガス状四塩化チタンを36Nm<sup>3</sup>/hrの窒素ガスで希釈した四塩化チタン希釈ガスを1,000℃に予熱し、36Nm<sup>3</sup>/hrの空気と25Nm<sup>3</sup>/hrの水蒸気を混合した酸化性ガスを1,000℃に予熱し、これらの原料ガスを石英ガラス製反応器に導入した。800℃以上1,100℃未満の高温滞留時間を0.02秒となるように冷却空気を反応管に導入後、ポリテトラフルオロエチレン製バグフィルターにて超微粒子状酸化チタン粉末を捕集した。

【0050】得られた酸化チタンを熱風循環加熱炉に入れ、水と酸化チタン質量比0.06、加熱温度350℃で脱塩素した。こうして得られた酸化チタンは、BET比表面積が97m<sup>2</sup>/g、ルチル含有率が1%、水抽出塩素含有率が1,800質量ppm、全塩素含有率が2,000質量ppmであった。式(1)に水抽出塩素含有量1,800質量ppm、全塩素含有量2,000質量ppmを代入して算出される表面塩素率は80%よりも高く、全塩素含有率は、式(2)に比表面積97m<sup>2</sup>/gを代入して算出される値よりも小さな数値を示した。この粉末のレーザー回折式粒度分布測定法にて測定した粒度分布における90%累積質量粒度分布径D90は2.2 $\mu$ mであった。ルチル化率、BET比表面積、全塩素含有量、表面塩素率、D90、及び、Fe、Al、Si、Sの分析結果を表1に示す。

【0051】比較例1：11.8Nm<sup>3</sup>/hrのガス状四塩化チタンを8Nm<sup>3</sup>/hrの窒素ガスで希釈した四塩化チタン希釈ガスを900℃に予熱し、8Nm<sup>3</sup>/hrの酸素と32Nm<sup>3</sup>/hrの水蒸気を混合した酸化性ガスを800℃に予熱し、これらの原料ガスを石英ガラス製反応器に導入した。800℃以上1,100℃未満の高温滞留時間を0.2秒となるように冷却空気を反応管に導入後、ポリテトラフルオロエチレン製バグフィルターにて超微粒子状酸化チタン粉末を捕集した。

【0052】得られた酸化チタンを円筒形回転式加熱炉に通し、水と酸化チタン質量比0.02、加熱温度450℃で脱塩素した。こうして得られた酸化チタンは、BET比表面積が19m<sup>2</sup>/g、ルチル含有率が11%、水抽出塩素含有量が300質量ppm、全塩素含有量が300質量ppmであった。式(1)に水抽出塩素含有量300質量ppm、全塩素含有量300質量ppmを代入して算出される表面塩素率は80%よりも高く、全塩素含有率は、式(2)に比表面積19m<sup>2</sup>/gを代入して算出される値よりも小さな数値を示した。この粉末のレーザー回折式粒度分布測定法にて測定した粒度分布における90%累積質量粒度分布径D90は

0.8 $\mu$ mであった。ルチル化率、BET比表面積、全塩素含有量、表面塩素率、D90、及び、Fe、Al、Si、Sの分析結果を表1に示す。

【0053】比較例2：4.7Nm<sup>3</sup>/hrのガス状四塩化チタンを36Nm<sup>3</sup>/hrの窒素ガスで希釈した四塩化チタン希釈ガスを800℃に予熱し、36Nm<sup>3</sup>/hrの空気と25Nm<sup>3</sup>/hrの水蒸気を混合した酸化性ガスを800℃に予熱し、これらの原料ガスを石英ガラス製反応器に導入した。該反応管温度を750℃に制御し、原料ガスを0.08秒滞留するように冷却空気を反応管に導入後、ポリテトラフルオロエチレン製バグフィルターにて超微粒子状酸化チタン粉末を捕集した。

【0054】得られた酸化チタンを熱風循環加熱炉に入れ、水と酸化チタン質量比0.04、加熱温度350℃で脱塩素した。こうして得られた酸化チタンは、BET比表面積が74m<sup>2</sup>/g、ルチル含有率が2%、水抽出塩素含有率が2,800質量ppm、全塩素含有率が3,900質量ppmであった。式(1)に水抽出塩素含有量2,800質量ppm、全塩素含有量3,900質量ppmを代入して算出される表面塩素率は80%よりも低く、全塩素含有率は、式(2)に比表面積74m<sup>2</sup>/gを代入して算出される値よりも大きな数値を示した。この粉末のレーザー回折式粒度分布測定法にて測定した粒度分布における90%累積質量粒度分布径D90は3.6 $\mu$ mであった。ルチル化率、BET比表面積、全塩素含有量、表面塩素率、D90、及び、Fe、Al、Si、Sの分析結果を表1に示す。

【0055】比較例3：5.9Nm<sup>3</sup>/hrのガス状四塩化チタンを30Nm<sup>3</sup>/hrの窒素ガスで希釈した四塩化チタン希釈ガスを1,100℃に予熱し、4Nm<sup>3</sup>/hrの酸素と16Nm<sup>3</sup>/hrの水蒸気を混合した酸化性ガスを1,100℃に予熱し、これらの原料ガスを石英ガラス製反応器に導入した。該反応管温度を1,200℃に制御し、原料ガスを0.04秒滞留するように冷却空気を反応管に導入後、ポリテトラフルオロエチレン製バグフィルターにて超微粒子状酸化チタン粉末を捕集した。

【0056】得られた酸化チタンを熱風循環加熱炉に入れ、水と酸化チタン質量比0.06、加熱温度450℃で脱塩素した。こうして得られた酸化チタンは、BET比表面積が44m<sup>2</sup>/g、ルチル含有率が12%、水抽出塩素含有量が1,200質量ppm、全塩素含有量が1,300質量ppmであった。式(1)に水抽出塩素含有量1,200質量ppm、全塩素含有量1,300質量ppmを代入して算出される表面塩素率は80%よりも高く、全塩素含有率は、式(2)に比表面積44m<sup>2</sup>/gを代入して算出される値よりも小さな数値を示した。この粉末のレーザー回折式粒度分布測定法にて測定した粒度分布における90%累積質量粒度分布径D90は1.2 $\mu$ mであった。ルチル化率、BET比表面



積、全塩素含有量、表面塩素率、D90、及び、Fe、Al、Si、Sの分析結果を表1に示す。

比較例4：市販の硫酸チタニル溶液（関東化学（株）製、試薬1級）を煮沸し、得られた沈殿を純水で洗浄し、含水酸化チタンを得た。この含水酸化チタンの残存硫酸を除去するため、純水を加えスラリーとし、これを攪拌しながらアンモニア水溶液を加えてpH5に調整し、12時間攪拌した。この後、限外ろ過膜で含水酸化チタン濃度を20質量%まで濃縮した。濃縮液に再びアンモニア水溶液を加えてpH5に調整し、12時間攪拌の後、純水を加えながら限外ろ過膜でろ過しチタニアゾルを得た。得られたチタニアゾルを300℃で2時間乾\*

\* 燥し、液相法による超微粒子酸化チタンを得た。得られた酸化チタンはBET比表面積が212m<sup>2</sup>/g、ルチル含有率1%であった。水抽出塩素含有量、全塩素含有量はともに0質量ppmであった。この酸化チタンを乳鉢で解砕し、レーザー回折式粒度分布測定法にて粒度分布を測定したところ、90%累積質量粒度D90は26.1μmであった。ルチル化率、BET比表面積、全塩素含有量、表面塩素率、D90、及び、Fe、Al、Si、Sの分析結果を表1に示す。

【0057】

【表1】

	実施例1	実施例2	実施例3	比較例1	比較例2	比較例3	比較例4
ルチル化率 %	1	3	1	11	2	12	1
BET比表面積 m <sup>2</sup> /g	22	65	97	19	74	44	212
全塩素含有量 質量 ppm	1,000	1,100	2,000	300	3,900	1,300	<10
表面塩素率 %	90	91	90	100	72	92	—
D90 μm	1.1	1.9	2.2	0.8	3.6	1.2	26.1
Fe 質量 ppm	<10	<10	<10	<10	<10	<10	50
Al 質量 ppm	<10	<10	<10	<10	<10	<10	<10
Si 質量 ppm	<20	<20	<20	<20	<20	<20	<20
S 質量 ppm	<10	<10	<10	<10	<10	<10	670

【0058】

【発明の効果】本発明により、同等のBET比表面積を有する従来の酸化チタンに比べ、粒子内部のハロゲン含有量が低く、分散性に特に優れた、気相法によるアナターゼ型の超微粒子酸化チタン、これを脱ハロゲンすることによりBET比表面積（B）とハロゲン含有率（C）との関係が前記式（2）の条件を満足する酸化チタン、レーザー回折式粒度分布測定法で測定されたD90が2.5μm以下の酸化チタン、及びこれらの製造方法が提供される。

【0059】本発明の酸化チタンは、光触媒用途や太陽電池用途等に好適であり、特に、水系の溶媒に対する分散性が優れるので、水中での光触媒用途に好適に用いることができ、粉体としても解砕工程等が不要もしくは極めて軽微な設備で済み、工業的に非常に大きな実用的価値を有するものである。

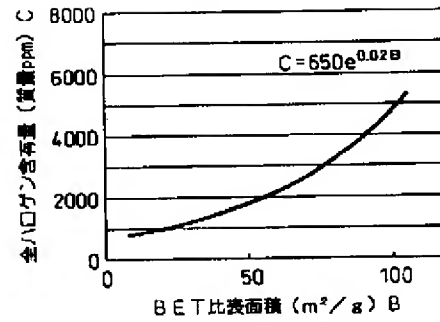
【図面の簡単な説明】

【図1】超微粒子状酸化チタンのハロゲン含有率とBET比表面積との関係を示す。

【図1】

図1

比表面積とハロゲン濃度



フロントページの続き

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